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(21) International Application Number: PCT/US93/02785 (22) International Filing Date: 25 March 1993 (25.03.93) (30) Priority data: 07/858,271 26 March 1992 (26.03.92) US (71) Applicant: DOWELANCO [US/US]; 9002 Purdue Road, Indianapolis, IN 46268-1189 (US). (72) Inventors: GALKA, Christopher, S. ; 1222 Redbrook Court, Apartment B, Indianapolis, IN 46229 (US). RIEDER, Brent, J. ; 510 North State Street, Greenfield, IN 46140 (US). SWAYZE, John, K. ; 4665 Cheval Place, Carmel, IN 46033 (US).		(74) Agent: STUART, Donald, R.; DowElanco Patent Department, 9002 Purdue Road, Indianapolis, IN 46268-1189 (US). (81) Designated States: AT, AU, BB, BG, BR, CA, CH, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, LK, LU, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT). Published <i>With international search report.</i>
(54) Title: N-HETEROCYCLIC NITRO ANILINES AS FUNGICIDES (57) Abstract Anilino heterocyclic compounds, e.g. 4-bromo-3-(4-fluorophenyl)-N-(2,4-dinitro-6-(trifluoromethyl)-phenyl)isothiazol-5-amine and N-(4-bromo-4-chloro-3-methyl-5(4H)-isothiazolyldene)-2,4-dinitro-6-(trifluoromethyl)benzenamine, exhibit fungicidal activity as well as insecticidal and nematocidal activity.		

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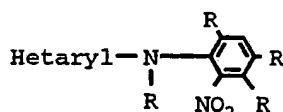
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N-heterocyclic nitro anilines as fungicides

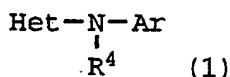
This invention provides new anilino heterocyclic compounds that are useful as agricultural chemicals. More specifically, the invention provides new anilino heterocyclic compounds that are useful as plant fungicides, new plant fungicide compositions utilizing the new compounds, and new methods of combating plant pathogens utilizing the new compounds and compositions.

European Patent Application 478,974A discloses insecticidal use of compounds of the formula



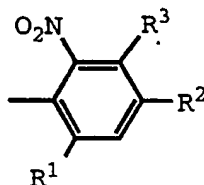
where hetaryl is thienyl, thiazolyl, isothiazolyl, or thiadiazolyl. There is no disclosure of fungicidal activity for these compounds.

In one aspect, the present invention provides a method of inhibiting plant pathogens which comprises applying an effective amount of a compound of formula (1):



or a salt thereof, wherein:

Ar is a group of the formula

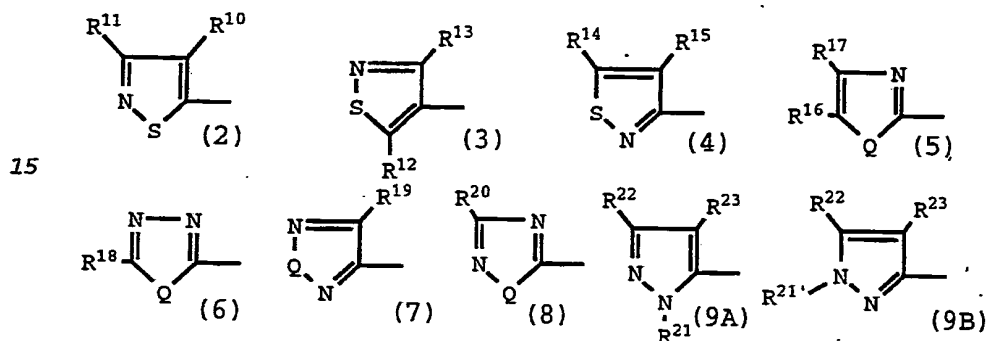


R^1 and R^2 are independently H, NO_2 , halo, $\text{C}_1\text{-C}_6$ alkyl, $\text{C}_1\text{-C}_6$ haloalkyl, $\text{C}_2\text{-C}_6$ alkenyl, $\text{C}_2\text{-C}_6$ alkynyl, $\text{C}_1\text{-C}_4$ alkylsulfonyl, phenylsulfonyl, substituted phenylsulfonyl, $\text{SO}_2\text{NR}^5\text{R}^6$, $\text{C}_1\text{-C}_4$ alkoxy, $\text{C}_1\text{-C}_4$ haloalkoxy, $\text{C}_1\text{-C}_4$ alkylthio, $\text{C}_1\text{-C}_4$ haloalkylthio, COOR^5 , or CN, provided R^1 is not CN, or

CONR⁵R⁶, where R⁵ and R⁶ are H, C₁-C₄ alkyl, C₃-C₇ alkenyl, C₃-C₇ cycloalkyl or cycloalkenyl, or R⁵ and R⁶ together with the nitrogen atom to which they are attached form a 5-7 member ring containing up to three additional heteroatoms selected from O, N, and S; R³ is H, halo, NR⁵R⁶, C₁-C₆ haloalkyl, C₁-C₆ alkoxy, C₁-C₆ haloalkoxy, C₁-C₆ alkylthio, C₁-C₆ haloalkylthio, phenoxy, substituted phenoxy, phenylthio, substituted phenylthio, benzyloxy, substituted benzyloxy, benzylthio, or substituted benzylthio;

10 R⁴ is H, COOR⁷, CONR⁵R⁶, CHO, COR⁷, or SO₂R⁷, SO₂NR⁵R⁶, where R⁵ and R⁶ are as defined above and R⁷ is C₁-C₈ alkyl, C₃-C₈ alkenyl, C₂-C₈ branched alkyl, C₁-C₄ haloalkyl, aralkyl, phenyl, or substituted phenyl;

Het is a group selected from:



where

Q is S or O;

20 R¹⁰ is H, halo, C₁-C₈ alkyl, C₂-C₈ alkenyl, C₂-C₈ alkynyl, C₃-C₈ branched alkyl or alkenyl, C₃-C₇ cycloalkyl or cycloalkenyl, NO₂, CN, SCN, CO₂H, CONR⁵R⁶ where R⁵ and R⁶ are as defined above, CO₂R⁷ where R⁷ is as defined above, or S(O)_mR⁷ where m is 0,1, or 2 and R⁷ are as defined above.

25 R¹¹ is H, halo, C₁-C₈ alkyl, C₂-C₈ alkenyl, C₂-C₈ alkynyl, C₃-C₈ branched alkyl or alkenyl, C₃-C₇ cycloalkyl or cycloalkenyl, aralkyl, (C₃-C₇ cycloalkyl)methyl, phenyl, substituted phenyl, pyridyl, substituted pyridyl, furyl, substituted furyl, thienyl, substituted thienyl, S(O)_mR⁷, OR⁷,

$$\text{NHR}^7, \text{NR}^5\text{R}^6, \text{NR}^7\text{R}^7, \text{NH}_2, \text{R}^5\text{R}^6\text{N}-\text{N}-\overset{\text{R}^5}{\text{---}}, \text{R}^7-\overset{\text{O}}{\underset{\text{Q}}{\text{C}}}-\overset{\text{R}^5}{\text{N}}-\overset{\text{R}^5}{\text{N}}-\text{---},$$

$$\text{R}^5\text{R}^6\text{N}-\overset{\text{R}^5}{\underset{\text{Q}}{\text{C}}}-\overset{\text{R}^5}{\text{N}}-\text{N}-\text{---}, \text{R}^7-\overset{\text{O}}{\underset{\text{O}}{\text{S}}}-\overset{\text{R}^5}{\text{N}}-\overset{\text{R}^5}{\text{N}}-\text{---};$$
 where m, Q, R⁵, R⁶, and R⁷ are as defined above;

R¹² is H, halo, CN, CO₂H, halo C₁-C₃ alkyl, phenyl,
 5 substituted phenyl, CONR⁵R⁶, or CO₂R⁷ where R⁵, R⁶, and R⁷ are as defined above;

R¹³ is H, halo, CN, CO₂H, halo C₁-C₃ alkyl, phenyl,
 substituted phenyl, CONR⁵R⁶, or CO₂R⁷ where R⁵, R⁶, and R⁷ are as defined above;

10 R¹⁴ is C₁-C₈ alkyl, C₂-C₈ alkenyl, C₂-C₈ alkynyl, C₃-C₈ branched alkyl or alkenyl, C₁-C₈ haloalkyl, phenyl, substituted phenyl, pyridyl, substituted pyridyl, thienyl, substituted thienyl, furyl, substituted furyl, or aralkyl;

15 R¹⁵ is H, halo, NO₂, CN, CO₂H, CONR⁵R⁶, or CO₂R⁷ where R⁵, R⁶, and R⁷ are as defined above;

R¹⁶ is H, halo, C₁-C₈ alkyl, C₂-C₈ alkenyl, C₂-C₈ alkynyl, C₃-C₆ branched alkyl or alkenyl, C₃-C₇ cycloalkyl or cycloalkenyl, C₁-C₈ haloalkyl, CN, NO₂, C₁-C₈ alkoxy, C₁-C₈ haloalkoxy, C₁-C₈ haloalkylthio, phenyl, substituted phenyl,
 20 thienyl, substituted thienyl, furyl, substituted furyl, pyridyl, substituted pyridyl, aralkyl, phenoxy, or substituted phenoxy;

R¹⁷ is H, halo, C₁-C₈ alkyl, C₂-C₈ alkenyl, C₂-C₈ alkynyl, C₃-C₆ branched alkyl or alkenyl, C₃-C₇ cycloalkyl or cycloalkenyl, C₁-C₈ haloalkyl, CN, NO₂, C₁-C₈ alkoxy, C₁-C₈ haloalkoxy, C₁-C₈ haloalkylthio, phenyl, substituted phenyl,
 25 thienyl, substituted thienyl, furyl, substituted furyl, pyridyl, substituted pyridyl, aralkyl, phenoxy, or substituted phenoxy;

30 R¹⁸ is H, halo, C₁-C₈ alkyl, C₂-C₈ alkenyl, C₂-C₈ alkynyl, C₃-C₆ branched alkyl or alkenyl, C₃-C₇ cycloalkyl or

cycloalkenyl, C₁-C₈ haloalkyl, CN, NO₂, C₁-C₈ alkoxy, C₁-C₈ haloalkoxy, C₁-C₈ haloalkylthio, phenyl, substituted phenyl, thienyl, substituted thienyl, furyl, substituted furyl, pyridyl, substituted pyridyl, aralkyl, phenoxy, or substituted phenoxy, S(O)_nR', where n is 0-3, and R' is H, C₁-C₈ alkyl, C₂-C₈ alkenyl, C₃-C₆ branched alkyl or alkenyl, phenyl, substituted phenyl, aralkyl, CF₃, or NR⁵R⁶ where R⁵ and R⁶ are as defined above;

R¹⁹ is C₁-C₈ alkyl, C₂-C₈ alkenyl, C₂-C₈ alkynyl, C₃-C₆ branched alkyl or alkenyl, C₃-C₇ cycloalkyl or cycloalkenyl, phenyl, substituted phenyl, or aralkyl;

R²⁰ is H, halo, C₁-C₈ alkyl, C₂-C₈ alkenyl, C₂-C₈ alkynyl, C₃-C₆ branched alkyl or alkenyl, C₃-C₇ cycloalkyl or cycloalkenyl, C₁-C₆ haloalkyl, pyridyl, substituted pyridyl, furyl, substituted furyl, thienyl, substituted thienyl, phenyl, or substituted phenyl;

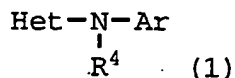
R²¹ and R^{21'} are C₁-C₈ alkyl, C₂-C₈ alkenyl, C₃-C₈ alkynyl, C₃-C₆ branched alkyl or alkenyl, C₃-C₇ cycloalkyl or cycloalkenyl, C₁-C₆ haloalkyl, pyridyl, substituted pyridyl, furyl, substituted furyl, thienyl, substituted thienyl, phenyl, or substituted phenyl, aralkyl, COR⁷, CR^{7'}R^{7'}COOR⁷, CR^{7'}R^{7'}CONR⁵R⁶, or S(O)_mR⁷, where m and R⁷ are as defined above and R^{7'} is H or C₁-C₃ alkyl;

R²² is H, C₁-C₈ alkyl, C₂-C₈ alkenyl, C₂-C₈ alkynyl, C₃-C₈ branched alkyl or alkenyl, C₃-C₇ cycloalkyl or cycloalkenyl, C₁-C₆ haloalkyl, aralkyl, C₁-C₆ alkoxy, C₁-C₆ haloalkoxy, C₁-C₆ alkylthio, C₁-C₆ haloalkylthio, (C₅-C₇ cycloalkyl)methyl, halo, CN, SCN, NO₂, NR⁵R⁶, phenyl, substituted phenyl, phenoxy, substituted phenoxy, pyridyl, substituted pyridyl, furyl, substituted furyl, thienyl, substituted thienyl; and

R²³ is H, halo, C₁-C₈ alkyl, C₂-C₈ alkenyl, C₂-C₈ alkynyl, C₃-C₈ branched alkyl or alkenyl, C₃-C₇ cycloalkyl or cycloalkenyl, C₁-C₆ haloalkyl, NO₂, CN, SCN, CO₂H, CONR⁵R⁶ where R⁵ and R⁶ are as defined above, CO₂R⁷, S(O)_mR⁷ where m

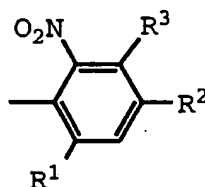
and R⁷ are as defined above, phenyl, substituted phenyl, pyridyl, substituted pyridyl, furyl, substituted furyl, thienyl, substituted thienyl, or aralkyl.

The invention also provides novel compounds of the
5 formula (1):



and salts thereof, wherein:

Ar is a group of the formula



10 R¹ and R² are independently H, NO₂, halo, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₂-C₆ alkenyl, C₂-C₆ alkynyl, C₁-C₄ alkylsulfonyl, phenylsulfonyl, substituted phenylsulfonyl, SO₂NR⁵R⁶, C₁-C₄ alkoxy, C₁-C₄ haloalkoxy, C₁-C₄ alkylthio, C₁-C₄ haloalkylthio, COOR⁵, or CN, provided R¹ is not CN, or
15 CONR⁵R⁶;

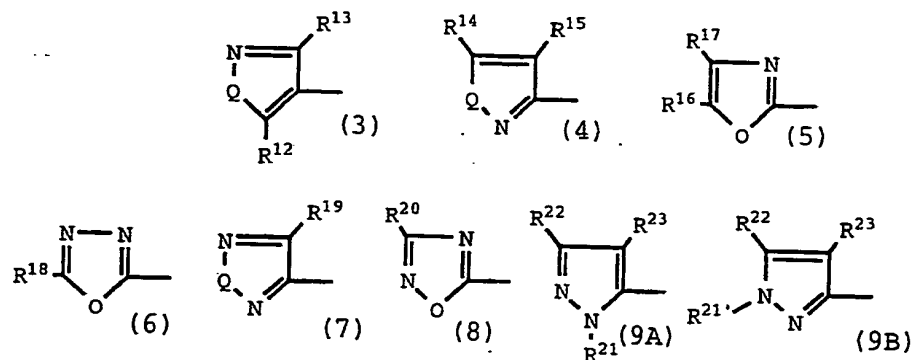
R³ is H, halo, NR⁵R⁶, C₁-C₆ haloalkyl, C₁-C₆ alkoxy, C₁-C₆ haloalkoxy, C₁-C₆ alkylthio, C₁-C₆ haloalkylthio, phenoxy, substituted phenoxy, phenylthio, substituted phenylthio, benzyloxy, substituted benzyloxy, benzylthio, or substituted
20 benzylthio;

R⁴ is H, COOR⁷, CONR⁵R⁶, CHO, COR⁷, SO₂R⁷, or SO₂NR⁵R⁶;

R⁵ and R⁶ are H, C₁-C₄ alkyl, C₃-C₇ alkenyl, C₃-C₇ cycloalkyl or cycloalkenyl, or R⁵ and R⁶ together with the nitrogen atom to which they are attached form a 5-7 member
25 ring containing up to three additional heteroatoms selected from O, N, and S;

R⁷ is C₁-C₈ alkyl, C₃-C₈ alkenyl, C₃-C₈ branched alkyl, C₁-C₄ haloalkyl, aralkyl, phenyl, or substituted phenyl;

Het is a group selected from:



where

5 Q is S or O;

R¹² is H, halo, CN, CO₂H, halo C₁-C₃ alkyl, phenyl, substituted phenyl, CONR⁵R⁶, or CO₂R⁷ where R⁵, R⁶, and R⁷ are as defined above;

10 R¹³ is H, halo, CN, CO₂H, halo C₁-C₃ alkyl, phenyl, substituted phenyl, CONR⁵R⁶, or CO₂R⁷ where R⁵, R⁶, and R⁷ are as defined above;

15 R¹⁴ is C₁-C₈ alkyl, C₂-C₈ alkenyl, C₂-C₈ alkynyl, C₃-C₈ branched alkyl or alkenyl, C₁-C₈ haloalkyl, phenyl, substituted phenyl, pyridyl, substituted pyridyl, thienyl, substituted thienyl, furyl, substituted furyl, or aralkyl;

R¹⁵ is H, halo, NO₂, CN, CO₂H, CONR⁵R⁶, or CO₂R⁷ where R⁵, R⁶, and R⁷ are as defined above;

20 R¹⁶ is H, halo, C₁-C₈ alkyl, C₂-C₈ alkenyl, C₂-C₈ alkynyl, C₃-C₆ branched alkyl or alkenyl, C₃-C₇ cycloalkyl or cycloalkenyl, C₁-C₈ haloalkyl, CN, NO₂, C₁-C₈ alkoxy, C₁-C₈ haloalkoxy, C₁-C₈ haloalkylthio, phenyl, substituted phenyl, thienyl, substituted thienyl, furyl, substituted furyl, pyridyl, substituted pyridyl, aralkyl, phenoxy, or substituted phenoxy;

25 R¹⁷ is H, halo, C₁-C₈ alkyl, C₂-C₈ alkenyl, C₂-C₈ alkynyl, C₃-C₆ branched alkyl or alkenyl, C₃-C₇ cycloalkyl or cycloalkenyl, C₁-C₈ haloalkyl, CN, NO₂, C₁-C₈ alkoxy, C₁-C₈

haloalkoxy, C₁-C₈ haloalkylthio, phenyl, substituted phenyl, thienyl, substituted thienyl, furyl, substituted furyl, pyridyl, substituted pyridyl, aralkyl, phenoxy, or substituted phenoxy;

5 R¹⁸ is H, halo, C₁-C₈ alkyl, C₂-C₈ alkenyl, C₂-C₈ alkynyl, C₃-C₆ branched alkyl or alkenyl, C₃-C₇ cycloalkyl or cycloalkenyl, C₁-C₈ haloalkyl, CN, NO₂, C₁-C₈ alkoxy, C₁-C₈ haloalkoxy, C₁-C₈ haloalkylthio, phenyl, substituted phenyl, thienyl, substituted thienyl, furyl, substituted furyl,
 10 pyridyl, substituted pyridyl, aralkyl, phenoxy, or substituted phenoxy, S(O)_nR', where n is 0-3, and R' is H, C₁-C₈ alkyl, C₂-C₈ alkenyl, C₃-C₆ branched alkyl or alkenyl, phenyl, substituted phenyl, aralkyl, CF₃, or NR⁵R⁶ where R⁵ and R⁶ are as defined above;

15 R¹⁹ is C₁-C₈ alkyl, C₂-C₈ alkenyl, C₂-C₈ alkynyl, C₃-C₆ branched alkyl or alkenyl, C₃-C₇ cycloalkyl or cycloalkenyl, phenyl, substituted phenyl, or aralkyl;

 R²⁰ is H, halo, C₁-C₈ alkyl, C₂-C₈ alkenyl, C₂-C₈ alkynyl, C₃-C₆ branched alkyl or alkenyl, C₃-C₇ cycloalkyl or
 20 cycloalkenyl, C₁-C₆ haloalkyl, pyridyl, substituted pyridyl, furyl, substituted furyl, thienyl, substituted thienyl, phenyl, or substituted phenyl;

 R²¹ and R^{21'} are C₁-C₈ alkyl, C₂-C₈ alkenyl, C₃-C₈ alkynyl, C₃-C₆ branched alkyl or alkenyl, C₃-C₇ cycloalkyl or
 25 cycloalkenyl, C₁-C₆ haloalkyl, pyridyl, substituted pyridyl, furyl, substituted furyl, thienyl, substituted thienyl, phenyl, substituted phenyl, aralkyl, COR⁷, CR^{7'}R^{7'}COOR⁷, CR^{7'}R^{7'}CONR⁵R⁶, or S(O)_mR⁷, where m, R⁵, R⁶, and R⁷ are as defined above, and R^{7'} is H or C₁-C₃ alkyl;

30 R²² is H, C₁-C₈ alkyl, C₂-C₈ alkenyl, C₂-C₈ alkynyl, C₃-C₈ branched alkyl or alkenyl, C₃-C₇ cycloalkyl or cycloalkenyl, C₁-C₆ haloalkyl, aralkyl, C₁-C₆ alkoxy, C₁-C₆ haloalkoxy, C₁-C₆ alkylthio, C₁-C₆ haloalkylthio, (C₅-C₇ cycloalkyl)methyl, halo, CN, SCN, NO₂, phenyl, substituted
 35 phenyl, phenoxy, substituted phenoxy, pyridyl, substituted

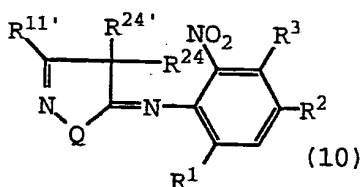
pyridyl, furyl, substituted furyl, thienyl, substituted thienyl, or NR^5R^6 where R^5 and R^6 are as defined above; and

R^{23} is H, halo, $\text{C}_1\text{-C}_8$ alkyl, $\text{C}_2\text{-C}_8$ alkenyl, $\text{C}_2\text{-C}_8$ alkynyl, $\text{C}_3\text{-C}_8$ branched alkyl or alkenyl, $\text{C}_3\text{-C}_7$ cycloalkyl or cycloalkenyl, $\text{C}_1\text{-C}_6$ haloalkyl, NO_2 , CN, SCN, CO_2H , CONR^5R^6 , CO_2R^7 , COR^7 , $\text{S(O)}_m\text{R}^7$, phenyl, substituted phenyl, pyridyl, substituted pyridyl, furyl, substituted furyl, thienyl, substituted thienyl, or aralkyl, where m, R^5 , R^6 , and R^7 are as defined above;

provided that the following compounds are excluded:

- a) 2-methyl-5-(2,4-dinitrophenylamino)-1,3,4-oxadiazole;
- b) N-methyl-5-trifluoromethyl-2-(2-chloro-4,6-dinitroanilino)-1,3,4-thiadiazole;
- c) N-methyl-5-t-butyl-2-(2-chloro-4,6-dinitroanilino)-1,3,4-thiadiazole;
- d) 3-(2,4-dinitroanilino)-4-nitro-5-phenylpyrazole; and
- e) 3-(2,6-dinitro-p-toluidino)-4-nitro-5-phenylpyrazole.

Another aspect of the invention comprises compounds having the following general formula (10):



wherein:

Q is S or O;

R^1 and R^2 are independently H, NO_2 , halo, $\text{C}_1\text{-C}_6$ alkyl, $\text{C}_1\text{-C}_6$ haloalkyl, $\text{C}_2\text{-C}_6$ alkenyl, $\text{C}_2\text{-C}_6$ alkynyl, $\text{C}_1\text{-C}_4$ alkylsulfonyl, phenylsulfonyl, substituted phenylsulfonyl, $\text{SO}_2\text{NR}^5\text{R}^6$, $\text{C}_1\text{-C}_4$ alkoxy, $\text{C}_1\text{-C}_4$ haloalkoxy, $\text{C}_1\text{-C}_4$ alkylthio, $\text{C}_1\text{-C}_4$ haloalkylthio, COOR^5 , CONR^5R^6 , or CN, provided R^1 is not CN;

R³ is H, halo, NR⁵R⁶, C₁-C₆ haloalkyl, C₁-C₆ alkoxy, C₁-C₆ haloalkoxy, C₁-C₆ alkylthio, C₁-C₆ haloalkylthio, phenoxy, substituted phenoxy, phenylthio, substituted phenylthio, benzyloxy, substituted benzyloxy, benzylthio, or substituted
5 benzylthio;

R⁵ and R⁶ are H, C₁-C₄ alkyl, C₃-C₇ alkenyl, C₃-C₇ cycloalkyl or cycloalkenyl, or R⁵ and R⁶ together with the nitrogen atom to which they are attached form a 5-7 member ring containing up to three additional heteroatoms selected
10 from O, N, and S;

R^{11'} is C₁-C₈ alkyl, C₂-C₈ alkenyl, C₂-C₈ alkynyl, C₃-C₈ branched alkyl or alkenyl, C₃-C₇ cycloalkyl or cycloalkenyl, aralkyl, (C₃-C₇ cycloalkyl)methyl, halo C₁-C₈ alkyl, phenyl, substituted phenyl, pyridyl, substituted pyridyl, furyl,
15 substituted furyl, thienyl, substituted thienyl; and

R²⁴ and R^{24'} are independently Cl or Br.

The invention also provides a method of inhibiting plant pathogens which comprises applying an effective amount of a compound of formula (10) to the locus of the pathogen.

20 The invention also provides a method of inhibiting a nematode population which comprises applying to the locus of a nematode, a nematode inactivating amount of a compound of the formula (1) or (10) as defined above.

The invention also provides a method of inhibiting an
25 insect or mite population which comprises applying to the locus of the insect or arachnid an effective insect or mite inactivating amount of a compound of formula (1) or (10).

Detailed Description of the Invention

Throughout this document, all temperatures are given in
30 degrees Celsius, and all percentages are weight percentages unless otherwise stated.

The term "halo" refers to a F, Cl, Br, or I atom.

The term "haloalkyl" refers to straight chain, branched chain, and cyclo groups.

The term "HPLC" refers to a high pressure liquid chromatography.

5 The term "substituted phenyl" refers to phenyl substituted with C₁-C₆ alkyl, C₂-C₇ alkenyl, C₂-C₇ alkynyl, C₃-C₇ branched alkyl, C₃-C₇ cycloalkyl, C₁-C₆ alkoxy, C₁-C₆ alkylthio, halo, hydroxy, NO₂, C₁-C₆ haloalkyl, C₁-C₆ haloalkoxy, C₁-C₆ haloalkylthio, CN, phenyl, substituted
10 phenyl, phenoxy, substituted phenoxy, C₁-C₄ alkanoyloxy, benzyloxy, or S(O)_mAlk, where m=0-2.

The terms "substituted benzyl", "substituted benzyloxy", and "substituted benzylthio" refer to such groups that are ring substituted with C₁-C₆ alkyl, C₂-C₇ alkenyl, C₂-C₇
15 alkynyl, C₃-C₇ branched alkyl, C₃-C₇ cycloalkyl, C₁-C₆ alkoxy, C₁-C₆ alkylthio, halo, hydroxy, NO₂, C₁-C₆ haloalkyl, C₁-C₆ haloalkoxy, C₁-C₆ haloalkylthio, CN, phenyl, substituted phenyl, phenoxy, substituted phenoxy, C₁-C₄ alkanoyloxy, benzyloxy, or S(O)_mAlk, where m=0-2.

20 The terms "substituted phenoxy" and "substituted phenylthio", and "substituted phenylsulfonyl" refer to such groups that are substituted with C₁-C₆ alkyl, C₂-C₇ alkenyl, C₂-C₇ alkynyl, C₃-C₇ branched alkyl, C₃-C₇ cycloalkyl, C₁-C₆ alkoxy, C₁-C₆ alkylthio, halo, hydroxy, NO₂, C₁-C₆ haloalkyl, C₁-C₆ haloalkoxy, C₁-C₆ haloalkylthio, CN, phenyl, substituted
25 phenyl, phenoxy, substituted phenoxy, C₁-C₄ alkanoyloxy, benzyloxy, or S(O)_mAlk, where m=0-2.

The term "aralkyl" refers to such groups wherein the aryl portion is phenyl or substituted phenyl and the alkyl portion
30 is C₁-C₃ straight chain or C₂-C₃ branched chain, e.g. $\begin{array}{c} \text{CH}_3 \\ | \\ -\text{CH}- \end{array}$, $\begin{array}{c} \text{CH}_3 \\ | \\ -\text{C}- \\ | \\ \text{CH}_3 \end{array}$, or $\begin{array}{c} \text{C}_2\text{H}_5 \\ | \\ -\text{CH}- \end{array}$.

Substituted pyridyl, substituted furyl, and substituted thienyl refer to such groups substituted with halo, halo C₁-C₄

alkyl, CN, NO₂, C₁-C₄ alkyl, C₃-C₄ branched alkyl, phenyl, (C₁-C₄) alkoxy, or halo (C₁-C₄) alkoxy.

The invention includes salts of the compounds of formulas 1, 10 and 10A. Specifically contemplated are compounds of those formulas wherein R⁴ is

(a) an alkali metal or alkaline earth metal ion such as sodium, potassium, calcium, magnesium, barium,

(b) an ammonium ion whose nitrogen can carry up to four C₁-C₄ alkyl, hydroxy C₁-C₄ alkyl, phenyl, substituted phenyl, benzyl, or substituted benzyl substituents,

(c) a phosphonium ion,

(d) a sulfonium ion,

(e) an equivalent of a transition metal cation, especially manganese, iron, copper, and zinc.

As will be apparent to those skilled in the art, for compounds having pyridyl, furyl, or thienyl as an optional substituent, as in the case where R¹⁸, R²⁰, or R²¹ is such a group, a variety of other heteroaryl groups are functionally equivalent to the named heteroaryl groups, and substitution of these equivalents is within the scope of the invention. A preferred heteroaryl group is 2-pyridyl.

Compounds of formula (1) wherein Het is a group of formula (2) are N-(substituted phenyl)-5-isothiazolamines.

Compounds of formula (1) wherein Het is a group of formula (3) and Q is S are N-(substituted phenyl)-4-isothiazolamines. Compounds of formula (1) wherein Het is a group of formula (3) and Q is O are N-(substituted phenyl)-4-isoxazolamines.

Compounds of formula (1) wherein Het is a group of formula (4) and Q is S are N-(substituted phenyl)-3-isothiazolamines. Compounds of formula (1) wherein Het is a

group of formula (4) and Q is O are N-(substituted phenyl)-3-isoxazolamines.

Compounds of formula (1) wherein Het is a group of formula (5) and Q is S are N-(substituted phenyl)-2-thiazolamines. Compounds of formula (1) wherein Het is a group of formula (5) and Q is O are N-(substituted phenyl)-2-oxazolamines.

Compounds of formula (1) wherein Het is a group of formula (6) and Q is S are N-(substituted phenyl)-1,3,4-thiadiazol-5-amines and N-(substituted phenyl)-1,3,4-thiadiazol-2-amines. Compounds of formula (1) wherein Het is a group of formula (6) and Q is O are N-(substituted phenyl)-1,3,4-oxadiazol-5-amines and N-(substituted phenyl)-1,3,4-oxadiazol-2-amines.

Compounds of formula (1) wherein Het is a group of formula (7) and Q is S are N-(substituted phenyl)-1,2,5-thiadiazol-3-amines. Compounds of formula (1) wherein Het is a group of formula (7) and Q is O are N-(substituted phenyl)-1,2,5-oxadiazol-3-amines.

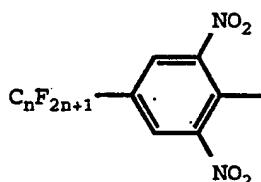
Compounds of formula (1) wherein Het is a group of formula (8) and Q is S are N-(substituted phenyl)-1,2,4-thiadiazol-5-amines. Compounds of formula (1) wherein Het is a group of formula (8) and Q is O are N-(substituted phenyl)-1,2,4-oxadiazol-5-amines.

Compounds of formula (1) wherein Het is a group of formula (9) are N-(substituted phenyl)-5-pyrazolamines.

Preferred Embodiments

The compounds of formulas (1) and (10) have demonstrated useful activity against plant pathogens, however certain classes of these compounds are preferred for reasons of greater efficacy. More specifically, the following classes of compounds are preferred:

- 1) isothiazole derivatives of formula (1) wherein Het is a group of formula (2);
- 2) compounds of class 1 wherein R^{10} is halo;
- 3) compounds of class 2 wherein R^{10} is bromo;
- 5 4) compounds of class 1 wherein R^{10} is iodo;
- 5) compounds of any one of classes 1 to 4 wherein R^{11} is C_1 - C_4 alkyl, C_3 - C_4 branched alkyl, C_3 - C_7 cycloalkyl, phenyl, or phenyl substituted with C_1 - C_4 alkyl, halo, C_1 - C_6 haloalkyl;
- 10 6) compounds of any one of classes 1 to 5 wherein Ar is a substituted phenyl group of the formula



wherein n is 1 or 2;

- 7) compounds of any one of classes 1 to 5 wherein Ar is DTI;
- 15 8) compounds of any one of classes 1 to 5 wherein Ar is o-DTI;
- 9) compounds of formula (10) wherein Ar is DTI;
- 10) compounds of formula (10) wherein R^{24} and $R^{24'}$ are
- 20 Cl.

The following specific compounds are preferred for their exceptional activity:

3-methyl-N-(2,4-dinitro-6-(trifluoromethyl)phenyl)isothiazol-5-amine;

4-bromo-3-methyl-N-(2,4-dinitro-6-(trifluoromethyl)phenyl)isothiazol-5-amine;

N-(4,4-dichloro-3-methyl-5(4H)-isothiazolylidene)-2,4-dinitro-6-(trifluoromethyl)benzenamine;

4-chloro-3-methyl-N-(2,4-dinitro-6-(trifluoromethyl)-phenyl)isothiazol-5-amine;

3-methyl-4-nitro-N-(2,4-dinitro-6-(trifluoromethyl)-phenyl)isothiazol-5-amine;

3-(3-methylphenyl)-N-(2,4-dinitro-6-(trifluoromethyl)-phenyl)isothiazol-5-amine;

4-bromo-3-ethyl-N-(2,4-dinitro-6-(trifluoromethyl)-phenyl)isothiazol-5-amine;

4-bromo-3-(3-methylphenyl)-N-(2,4-dinitro-6-(trifluoromethyl)phenyl)isothiazol-5-amine;

3-t-butyl-N-(2,6-dinitro-4-(trifluoromethyl)phenyl)-isothiazol-5-amine;

4-bromo-3-t-butyl-N-(2,4-dinitro-6-(trifluoromethyl)-phenyl)isothiazol-5-amine;

4-bromo-3-methyl-N-(2,6-dinitro-4-(trifluoromethyl)-phenyl)isothiazol-5-amine;

N-(4-bromo-4-dichloro-3-ethyl-5(4H)-isothiazolylidene)-2,4-dinitro-6-(trifluoromethyl)benzenamine;

N-(4,4-dichloro-3-n-butyl-5(4H)-isothiazolylidene)-2,4-dinitro-6-(trifluoromethyl)benzenamine;

N-(4,4-dibromo-3-methyl-5(4H)-isothiazolylidene)-2,4-dinitro-6-(trifluoromethyl)benzenamine;

4-bromo-3-ethyl-N-(2,6-dinitro-4-(trifluoromethyl)-phenyl)isothiazol-5-amine;

4-chloro-3-methyl-N-(2,6-dinitro-4-(trifluoromethyl)-phenyl)isothiazol-5-amine;

N-(4,4-dichloro-3-t-butyl-5(4H)-isothiazolylidene)-2,6-dinitro-4-(trifluoromethyl)benzenamine;

4-chloro-3-t-butyl-N-(2,6-dinitro-4-(trifluoromethyl)-phenyl)isothiazol-5-amine;

3-methyl-4-iodo-N-(2,6-dinitro-4-(trifluoromethyl)-phenyl)isothiazol-5-amine;

3-t-butyl-4-bromo-N-(2,6-dinitro-4-(trifluoromethyl)-phenyl)isothiazol-5-amine;

4-bromo-3-cyano-N-(2,6-dinitro-4-(trifluoromethyl)-phenyl)isothiazol-5-amine;

1-(3-trifluoro-methylphenyl)-4-cyano-N-(2,6-dinitro-4-(trifluoro-methyl)phenyl)pyrazol-5-amine;

N-(2,6-dinitro-4-(trifluoromethyl)phenyl)-2-phenyl-1,2,4-thiadiazol-5-amine;

N-(2,6-dinitro-4-(trifluoromethyl)phenyl)-2-phenyl-1,3,4-thiadiazol-5-amine;

N-(2,6-dinitro-4-(trifluoromethyl)phenyl)-4-phenyl--thiazol-2-amine;

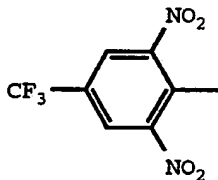
N-(2,6-dinitro-4-(trifluoromethyl)phenyl)-3-phenyl-isoxazol-5-amine;

N-(2,6-dinitro-4-(trifluoromethyl)phenyl)-4-bromo-3-phenylisoxazol-5-amine;

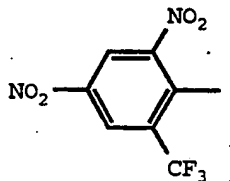
3-t-butyl-4-bromo-N-(2,6-dinitro-4-cyanophenyl)-isothiazol-5-amine;

1-(3-nitrophenyl)-4-phenyl-N-(2,6-dinitro-4-(trifluoromethyl)phenyl)pyrazol-5-amine.

The following tables identify representative compounds of formulas (1) and (10), together with characterizing physical and biological activity. Abbreviations used in the table include the following: \emptyset refers to phenyl, Me refers to methyl, Et refers to ethyl, n-Bu refers to n-butyl, t-Bu refers to t-butyl, Bz refers to benzyl. The term "DTI" refers to the group

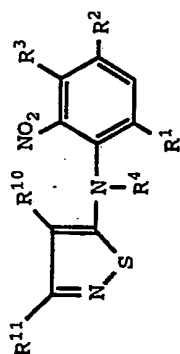


The term "o-DTI" refers to the group










An explanation of the biological data reported in the table is given hereinafter in the section titled "Greenhouse Tests."

Table 1A



Compound	R10	R11	R1	R2	R3	R4	melting point °C	POWD MDEW	RICE BLAST	LEAF RUST	DOWN MDEW SQUASH	LEAF BLOT	DOWN MDEW GRAPE
1	Br	1-Pr	CF3	NO2	H	H	oil	+++4 3G	++1 3G	+++8 3G		-1 3G	+++7 5G
2	Br	Me	CF3	NO2	H	H	<40	+++1 3G	+++1 3G	+++7 3G	+++5 3G		
3	Br	Et	CF3	NO2	H	H	87-91	+++5 3G	-	+++7 3G	+++9 4G		
4	Br	n-Bu	CF3	NO2	H	H	oil	++1	-	+++1	+++1		
5	Br	t-Bu	CF3	NO2	H	H	40	++ 3G	3G	+++6 3G	+++4 3G		
6	Br	3-MeØ	CF3	NO2	H	H	150-153	-	-	+++5 2G	+++6		
7	Cl	Me	CF3	NO2	H	H	104-107.5	+++1 3G	-	+++8 3G	+++8 3G		
8	Cl	t-Bu	CF3	NO2	H	H	oil	+++2	+++2 3G	+++8 3G	+++6 2G		
9	Cl	-CH2-C6H11	CF3	NO2	H	H	oil	++	+	+++		-	+++ 2G
10	H	1-Pr	CF3	NO2	H	H	oil						
11	H	Me	CF3	NO2	H	H	118-120	+	-	+++7 3G	+++6 2G		
12	H	1-Pr	CF3	NO2	H	H	oil						
13	H	n-Bu	CF3	NO2	H	H	oil	+++1	-	+++7 2G	+		
14	H	t-Bu	CF3	NO2	H	H	98-102	+	3G	3G	+++ 3G		
15	H	t-Bu	CF3	NO2	H	Me	oil	+++2	++	++	++		

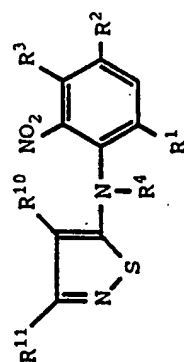
Compound	R ¹⁰	R ¹¹	R ¹	R ²	R ³	R ⁴	melting point °C	POWD MDEW	RICE BLAST	LEAF RUST	DOWN SQUASH MDEW	LEAF BLOT	DOWN MDEW GRAPE
16	H	3-MeO	CF ₃	NO ₂	H	H	60-65	-	-	-	+++8	++	+++
17	I	-CH ₂ -C ₆ H ₁₁	CF ₃	NO ₂	H	H	<50	+	2G	+++		2G	3G
18	I	n-Bu	CF ₃	NO ₂	H	H	oil	+++1 3G	-	+++5 3G		-	++ 5G
19	NO ₂	Me	CF ₃	NO ₂	H	H		-	-	+++8 2G	+++7 3G		
20	NO ₂	t-Bu	CF ₃	NO ₂	H	H	106-109	+++1 3G	-	+++7 3G		-	+++7
21	Br	Me	H	CF ₃	H	H	154-155	-	-	-		-	-
22	Br	Me	NO ₂	C ₂ F ₅	H	H	103-105	+++3 2G	+++3 2G	+++7 2G		++ 2G	+++5 2G
23	H	Me	NO ₂	C ₂ H ₅	H	H	86.5-88	+++1	+++1	+++1		-	+++1
24	Br		NO ₂	CF ₃	H	H	161	+	+++4 3	+++7 8		+++1 5	+++8 9
25	Br		NO ₂	CF ₃	H	H							
26	Br		NO ₂	CF ₃	H	H							
27	Br		NO ₂	CF ₃	H	H							
28	Br		NO ₂	CF ₃	H	H							
29	Br	4-BrO	NO ₂	CF ₃	H	H							
30	Br	4-CH ₃ O	NO ₂	CF ₃	H	H							
31	Br	4-Me ₂ N	NO ₂	CF ₃	H	H							
32	Br	4-CN	NO ₂	CF ₃	H	H							
33	H		NO ₂	CF ₃	H	H	70-75	+++1 12G	+++1 3	+++1 72G		-1 1	+++1 9
34	H		NO ₂	CF ₃	H	H							

Compound	R ¹⁰	R ¹¹	R ¹	R ²	R ³	R ⁴	melting point °C	Powd MDEW	RICE BLAST	LEAF RUST	SQUASH	DOWN MDEW	LEAF BLOT	DOWN MDEW
35	H		NO ₂	CF ₃	H	H								
36	H		NO ₂	CF ₃	H	H								
37	H		NO ₂	CF ₃	H	H								
38	H	4-BrØ	NO ₂	CF ₃	H	H								
39	H	4-Me ₂ NØ	NO ₂	CF ₃	H	H								
40	H	4-CNØ	NO ₂	CF ₃	H	H								
41	Br	Ø	NO ₂	CF ₃	H	H	150-152	++1 2G	++3 2G	+++6 2G			+++1 2G	+++9 2G
42	H	4-CH ₃ OØ	NO ₂	CF ₃	H	H		-	-	+			+	++
43	Br	3-ClØ	NO ₂	CF ₃	H	H	112-114	+	+	+++			+++4 2G	+++7 2G
44	Br	4-CH ₃ OØ	NO ₂	CF ₃	H	H	178-180	+++1 2G	+++1	+++1 2G			-	+++1
45	Br	3-CH ₃ OØ	NO ₂	CF ₃	H	H	107-110	+1	+1	+1			++	+++1
46	Br	2-CH ₃ OØ	NO ₂	CF ₃	H	H	136-138	+1	+1	+1			+++1	+++1
47	Br	3-Br-4-(NMe ₂)Ø	NO ₂	CF ₃	H	H	124-125							
48	Br	Me	NO ₂	CF ₃	H	H	171-172	-	+++	+++	+++	+++	+++	+++
49	Br	Me	NO ₂	CF ₃	H	Ac	136-139	++	++	+++			-	+++
50	Br	Me	NO ₂	CF ₃	H	Me	181-184	-	-	-				-
51	Br	Et	NO ₂	CF ₃	H	H	99-103	++	+++	+++	+++	+++		
52	Br	1-Pr	NO ₂	CF ₃	H	H	136.5-138.5	+++	+++	+++	+++	+++	++	+++
53	Br	1-MePr	NO ₂	CF ₃	H	H	97-100							
54	Br	2-MePr	NO ₂	CF ₃	H	H	oil	+++5	+++3	+++7			+++1	+++9
55	Br	n-Bu	NO ₂	CF ₃	H	H	83-85	+++	+++	+++	+++	+++	+++	+++
56	Br	t-Bu	NO ₂	CF ₃	H	H	119-121	+++7	+++7	+++8			+++7	+++7
57	Br	-CH ₂ -C ₆ H ₁₁	NO ₂	CF ₃	H	H	oil	+	+	+++			++	+++

Compound	R ¹⁰	R ¹¹	R ¹	R ²	R ³	R ⁴	melting point °C	POWD MDEW	RICE BLAST	LEAF RUST	DOWN MDEW SQUASH	LEAF BLOT	DOWN MDEW GRAPE
58	Br	4-Cl \emptyset	NO ₂	CF ₃	H	H	192-194	++	+	+++		+	+++
59	Br	4-F \emptyset	NO ₂	CF ₃	H	H	132-133.5	++	++	+++		+++	+++
60	Cl	Me	NO ₂	CF ₃	H	H	138-142	++	+	+++	+++		
61	Cl	Me	NO ₂	CF ₃	H	Me	172-174.5	-	-	-			-
62	Cl	i-Pr	NO ₂	CF ₃	H	H	122-123	+++ 2G	+++	+++ 2G		++ 2G	+++
63	Cl	t-Bu	NO ₂	CF ₃	H	H	119-121.5	+++6	+++5	+++6	+++3	+++3	
64	Cl	-CH ₂ -C ₆ H ₁₁	NO ₂	CF ₃	H	H	84-86	++	++	+++		++	+++
65	Cl	4-F \emptyset	NO ₂	CF ₃	H	H	115-118	+++1	++3	+++3		+++1	+++9 2G
66	CN	Me	NO ₂	CF ₃	H	H	150-152	+	+	++ 2G		- 2G	++ 3G
67	CN	t-Bu	NO ₂	CF ₃	H	H	218-219.5	+	+	+++		-	+++ 2G
68	H	Me	NO ₂	CF ₃	H	H	118-120	+	++	+++	++		
69	H	Me	NO ₂	CF ₃	H	Me	147-149	-	-	-			+
70	H	i-Pr	NO ₂	CF ₃	H	H	127-128	+	+	++3		-	++
71	H	n-Bu	NO ₂	CF ₃	H	H	87-90	-	+	+++	+++		
72	H	t-Bu	NO ₂	CF ₃	H	H	112-114	++	-	+++	+++ 2C		
73	H	-CH ₂ -C ₆ H ₁₁	NO ₂	CF ₃	H	H	34-36	-	+	++		-	+++9
74	H	3-Me \emptyset	NO ₂	CF ₃	H	H	111-114	-	++	+	+++	++	+++
75	H	3-CH ₃ O \emptyset	NO ₂	CF ₃	H	H	121-124	-	+	+	+++	+	+++
76	H	4-Cl \emptyset	NO ₂	CF ₃	H	H	208-210	+	+	+++		-	+++
77	H	4-F \emptyset	NO ₂	CF ₃	H	H	195-198	++	+	++		-	+++
78	I	Me	NO ₂	CF ₃	H	H	177-178.5	-1	+++6	+++8		+++5	+++9
79	I	i-Pr	NO ₂	CF ₃	H	H	148-150	+	+++3	+++3		+++1	+++9
80	I	-CH ₂ -C ₆ H ₁₁	NO ₂	CF ₃	H	H	94-97	+	++	+++		+++	+++
81	I	4-F \emptyset	NO ₂	CF ₃	H	H	132-135	+	+	+++4		+++1	+++7
82	NO ₂	Me	NO ₂	CF ₃	H	H	175-178	+	++	+++		-	+++ 3G
83	NO ₂	i-Pr	NO ₂	CF ₃	H	H	136-137.5	++ 3G	+	+++ 3G		++ 3G	+++ 3G
84	NO ₂	4-F-3-NO ₂ - \emptyset	NO ₂	CF ₃	H	H	182-185	-	-	++		-	+++5

Compound	R ¹⁰	R ¹¹	R ¹	R ²	R ³	R ⁴	melting point °C	POWD MDEW	RICE BLAST	LEAF RUST	DOWN MDEW SQUASH	LEAF BLOT	DOWN MDEW GRAPE
85	Br	Me	NO ₂	CF ₃	Cl	H	149-151	-	++1	+++4		+	+++1 4G
86	H	Me	NO ₂	CF ₃	Cl	H	86-87.5	-	+	+		-	-
87	H	t-Bu	NO ₂	CF ₃	Cl	H	147-150	-	+++ 1	+++ 1	+++ 1		
88	Br	t-Bu	NO ₂	CF ₃	Cl	H	131-133	-	-	+++ 5	+++ 1		
89	Br	Me	NO ₂	Cl	H	H	144-146	-	+1	+++1		-	++
90	Br	Me	NO ₂	CN	H	H	180-183	-	+1	+++3		-	+++1
91	H	Me	NO ₂	CN	H	H	145-147	+1 2G	+1 2G	+1 2G		-	+++1
92	H	Me	NO ₂	CONH ₂	H	H	206-209	-	-	-		-	+++1
93	H	t-Bu	NO ₂	H	H	H	135-136	+	-	-		-	-
94	Br	Me	NO ₂	Me	H	H	147.5-149	+1	-	+1		-	-
95	Br	Me	NO ₂	NO ₂	H	H	133-134.5	-	-	+++5 3G		-	+++1 2G
96	Br	t-Bu	NO ₂	NO ₂	H	H	129-132	+	+	+++7 3G		-	+++ 4G
97	Cl	t-Bu	NO ₂	NO ₂	H	H	131-133	+	-	+++6 4G		-	+++ 4G
98	NO ₂	Me	NO ₂	NO ₂	H	H	175-178	-	-	-		-	+++3 2G
99	H	t-Bu	NO ₂	NO ₂	H	H	180-182	-	+	+	+++ 1		
100	Br	Me	NO ₂	t-Bu	H	H	188-192	+	-	-		-	-
101	H	Me	NO ₂	t-Bu	H	H	oil	-	-	-		-	-
102	Br	Me	t-Bu	NO ₂	H	H	137-139	++ 2G	++ 2G	+++5 2G		++ 3G	+++72G 4G
103	H	Me	t-Bu	NO ₂	H	H	165-167	-	-	-		-	+

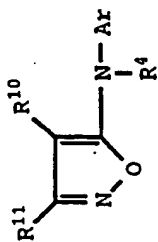
Table 1B



Compound	R ¹⁰	R ¹¹	R ¹	R ²	R ³	R ⁴	melting point °C	POWD MDEW	RICE BLAST	LEAF RUST	DOWN SQUASH MDEW	LEAF BLOT	DOWN MDEW GRAPE
208	Br	Me	NO ₂	CF ₃	H	H	170-172						
209	Br	t-Bu	NO ₂	CN	H	H	130-131	-1 12G	++3 62G	+++6 82G		++1 6	+++8 92G
210	I	t-Bu	NO ₂	CF ₃	H	H	128-130	+++1 8	+++1 8	+++6 8		++1 5	+++4 9
211	I	Ø	NO ₂	CF ₃	H	H	173-175	+++1 2	+++1 6	+++6 8		++1 4	+++1 92G
212	H	1-Pr	NO ₂	CF ₃	H	acetyl	112-115	-1 1	-1 1			++1 1	+++1 9
213	Me	Et	NO ₂	CF ₃	H	H	113-114	+++1 1	+++1 1	+		-1 1	++1 1
214	F	Me	NO ₂	CF ₃	H	H	82-84	+++1 1	+++1 1	++ 2G		-1 1	+++1 62G
215	Br	Me	NO ₂	CF ₃	H	Na	220-225	-1 4	+++5 8	+++7 8	+++7 9	+++3 8	+++3 9
216	Br	Me	NO ₂	CF ₃	H	K	143-146						
217	-SCF ₃	Me	NO ₂	CF ₃	H	H	138-140						
218	H	Pr	NO ₂	CF ₃	H	H	100-101	+++1 6	-1 1	++		++1 6	+++1 1
219	Br	4-MeOØ	NO ₂	CF ₃	H	H	186-187	+++1 1	-1 1	-		-1 1	-1 1
220	H	4-MeOØ	NO ₂	CF ₃	H	H	183-184	-1 1	-1 1	++1 1		++1 1	+++1 6

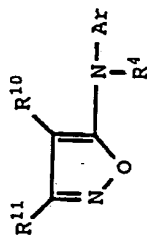
Compound	R ¹⁰	R ¹¹	R ¹	R ²	R ³	R ⁴	melting point °C	POWD MDEW	RICE BLAST	LEAF RUST	DOWN MDEW SQUASH	LEAF BLOT	DOWN MDEW GRAPE
221	Br	cyclopropyl	NO ₂	CF ₃	H	H	161	+1 3	++4 6	+++7 8		++1 5	+++8 9
222	H	cyclopropyl	NO ₂	CF ₃	H	H	70-75	++1 12G	++1 3	+++1 72G		-1 1	+++1 9

Table 2A



Compound	R ¹⁰	R ¹¹	Ar	R ⁴	melting point °C	POWD MDEW	RICE BLAST	LEAF RUST	DOWN MDEW SQUASH	LEAF BLOT	DOWN MDEW GRAPE
104	H	t-Bu	DTI	H	163-165	-	-	+	+		
105	H	CF ₃	o-DTI	H	131-134	+	2G	3G	+		
106	H	t-Bu	o-DTI	H	125-127.5	-	3G	3G	+++ 2G		
107	Br	t-Bu	o-DTI	H	gum	+	-	+++1 2C/3G	+++2		
108	H	C ₂ F ₄ H	DTI	H	148-149.5	+++1	+1	+++1		-	++
109	Br	C ₂ F ₄ H	DTI	H	oil	+++1 2G	+1	+++1 2G		+1 2G	+++1 2G
110	H	Ø	DTI	H		-1	+++1	+++3		+++1	+++7
111	Br	Ø	DTI	H		-1	+++1	+++1		+++1	+++6
112	H	1-Et-1-Me-Pr	DTI	H		-	+++1	+++1			+++1

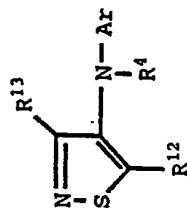
Table 2B



Compound	R ¹⁰	R ¹¹	Ar	R ⁴	melting point °C	POWD MDEW	RICE BLAST	LEAF RUST	DOWN MDEW SQUASH	LEAF BLOT	DOWN MDEW GRAPE
223	H	4-Cl \emptyset	DTI	H	184-185	-1 1	+1 3	-		++1 1	+++1 7
224	Br	1-Et-1-MePr	DTI	H	137-138	+1 2	+1 3	+		++1 1	+++1 6
225	H	4-CF ₃ \emptyset	DTI	H	190-192	-1 1	+1 2	-		+1 1	+++1 5
226	Br	4-CF ₃ \emptyset	DTI	H	125-128	+1 1	+1 1	+		+1 3	+1 42G
227	H	3-Cl \emptyset	DTI	H	180-182	-1 1	+1 2	++		++1 4	+++1 9
228	Br	4-Cl \emptyset	DTI	H	173-175	+1 1	-1 1	++		+1 1	+++1 52G
229	H	4-F \emptyset	DTI	H	152-155	++1 6	+1 4	++		++1 1	+++1 3
230	Cl	\emptyset	DTI	H	138-140	+1 1	+1 1	+		+1 1	+++1 62G
231	I	\emptyset	DTI	H	168-170	-1 1	+1 1	+		+1 1	+++1 9
232	Br	3-Cl \emptyset	DTI	H	100-101	-1 1	-1 1			++1 1	+++1 62G
233	Cl	1-Et-1-MePr	DTI	H	75-78	+++1 8	+++1 6	++		+++1 7	+++1 6
234	I	1-Et-1-MePr	DTI	H	170-175	-	-	+		-	+++1 4

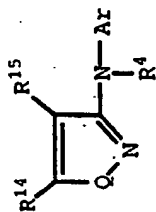
Compound	R ¹⁰	R ¹¹	Ar	R ⁴	melting point °C					SQUASH		GRAPE	
						POWD MDEW	RICE BLAST	LEAF RUST	DOWN MDEW	LEAF BLOT	DOWN MDEW		
235	Cl	t-Bu	DTI	H	136-137	+++1 9	++1 6	++		+++1 7	+++1 8		
236	Br	t-Bu	DTI	H	147-148	+++1 8	++1 5	++		+++1 7	+++1 9		
237	I	t-Bu	DTI	H	178-179	+1 4	+1 1	++		-1 1	+++1 9		
238	H	2-ClØ	DTI	H	174-175	-1 1	-1 1	+		-1 1	+++1 8		

Table 3



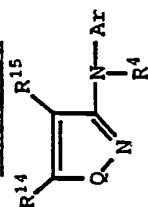
Compound	R ¹³	R ¹²	Ar	R ⁴	melting point °C	POWD MDEW	RICE BLAST	LEAF RUST	DOWN MDEW SQUASH	LEAF BLOT	DOWN MDEW GRAPE
113	CO ₂ NH ₂	CO ₂ Me	DTI	H		-	+++6 4G	+		-	++
114	CN	CO ₂ Et	DTI	H		+++3 4G	+++6 4G	+++8 4G		+++4 4G	+++9 3G
115	CN	CO ₂ Me	DTI	H							
116	3-CF ₃ Ø	CO ₂ Me	DTI	H	154-156						

Table 4A



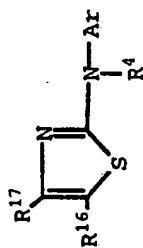
Compound	Q	R ¹⁴	R ¹⁵	Ar	R ⁴	melting point °C	POWD MDEW	RICE BLAST	LEAF RUST	DOWN MDEW SQUASH	LEAF BLOT	DOWN MDEW GRAPE
117	S	t-Bu	Br	DTI	H	132-135	+1	-1	+++4		-1	++1
118	S	t-Bu	Cl	DTI	H	95-101	+++1	-1	++1		-	+++1
119	S	t-Bu	H	o-DTI	H	98-101	++1	+++1	++3		+++1	+++5
120	S	t-Bu	Br	o-DTI	H	120-121	+++1	++1	+++3		+1	+++4
121	S	t-Bu	Cl	o-DTI	H	116-117	++1	2G	2G		2G	3G
122	O	t-Bu	H	DTI	H	140-142	3G	+1	+++5		+	+++1
123	O	T-Bu	H	DTI	Me	oil		2G	3G			3G

Table 4B



Compound	Q	R ¹⁴	R ¹⁵	Ar	R ⁴	melting point °C	POWD MDEW	RICE BLAST	LEAF RUST	DOWN MDEW SQUASH	LEAF BLOT	DOWN MDEW GRAPE
239	O	4-CF ₃ Ø	H	DTI	H	204-205	-1 1	+1 1	- -	- -	-1 1	-1 1
240	O	Ø	H	DTI	H	175-176	-1 1	-1 1	- -	- -	+1 1	-1 1

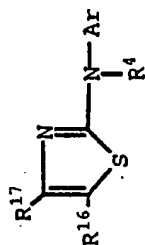
Table 5A



Compound	R ¹⁶	R ¹⁷	Ar	R ⁴	melting point °C	POWD MDEW	RICE BLAST	LEAF RUST	DOWN MDEW SQUASH	LEAF BLOT	DOWN MDEW GRAPE
124	Ø	CF ₃	o-DTI	H	121-122.5	-	-	+	+++7 2G		
125	3-CF ₃ Ø	CF ₃	DTI	H	175-177	+	+	++1	+		
126	3-CF ₃ Ø	CF ₃	o-DTI	H	110-117	+	+	+	+++1		
127	H	CF ₃	DTI	H	140-142	+++1 2G	+++1 2G	+++1 2G		+	+++6 2G
128	Br	CF ₃	DTI	H	160.5- 162.5	+++1	+++1	+++7		+1	+++9 3G
129	CN	t-Bu	DTI	H	212-214	+++1 3G	+1 2G	+++6 3G		-	+++1 2G
130	H	t-Bu	DTI	H		+++1	+1	+1		+1	+++1
131	Br	t-Bu	DTI	H		+++1	+++1	+++1		+++1	+++1
132	H	Ø	DTI	H		-	-	+		+	+++9
133	Br	Ø	DTI	H							
134	Cl	Ø	DTI	H							
135	H	3-ClØ	DTI	H	147	-	+	+		-	+++1
136	Br	3-ClØ	DTI	H		-	++	+++		++	+++3
137	Cl	3-ClØ	DTI	H							
138	H	4-ClØ	DTI	H		-1	+++1	+++1		+1	+++1
139	Br	4-ClØ	DTI	H							
140	Cl	4-ClØ	DTI	H							
141	H	3,4- Cl ₂ Ø	DTI	H		-1	+1	+++1		+++1	+++1
142	Br	3,4- Cl ₂ Ø	DTI	H							

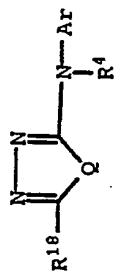
Compound	R16	R17	Ar	R4	melting point °C	POWD MDEW	RICE BLAST	LEAF RUST	SQUASH DOWN MDEW	LEAF BLOT	DOWN MDEW
143	Cl	3,4- Cl ₂ Ø	DTI	H							
144	H	4-BrØ	DTI	H		-	+1	++1		-1	++1
145	Br	4-BrØ	DTI	H		+1	++1	++1		++1	++1
146	Cl	4-BrØ	DTI	H							

Table 5B



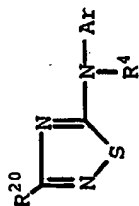
Compound	R ¹⁶	R ¹⁷	Ar	R ⁴	melting point °C	POWD MDEW	RICE BLAST	LEAF RUST	DOWN MDEW SQUASH	LEAF BLOT	DOWN MDEW GRAPE
241	H	4-Cl \emptyset	DTI	H		-1 1	++1 7	++1 5		+1 1	++1 4
242	H	\emptyset	DTI	H	53 dec	-1 1	-1 1	+1 5		+1 2	+++9 9
243	Br	\emptyset	DTI	H	64 dec	-1 1	+1 5	++3 8		++1 1	+++1 9
244	H	3-Cl- 4-(4- Cl \emptyset) \emptyset	DTI	H	199-200	-1 1	-1 1	-1 1		-1 1	+1 6
245	Br	4-Cl \emptyset	DTI	H	154-155	-1 1	+1 5	+++1 7		++1 6	+++1 9
246	CN	3-Cl \emptyset	DTI	H	183-184	+1 12G	+1 22G	+++7 82G		-1 12G	+++8 93G
247	Me	3-Cl- 4-Me \emptyset	DTI	H	137-139	-1 1	-1 1	-		-1 1	-1 1
248	4-Me \emptyset	4-Cl \emptyset	DTI	H	187-188	-1 1	-1 1	-		-1 1	-1 1
249	\emptyset	CF ₃	DTI	H	167-169						

Table 6A



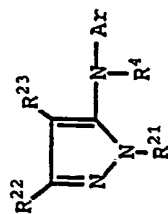
Compound	Q	R ¹⁸	Ar	R ⁴	melting point °C	POWD MDEW	RICE BLAST	LEAF RUST	DOWN MDEW SQUASH	LEAF BLOT	DOWN MDEW GRAPE
147	S	CF ₃	DTI	H	180-183	+++4	-	++3	+	++1 3G	+++1 2G
148	S	C ₂ F ₅	DTI	H	145-148	+	-	++			
149	S	CF ₃	o-DTI	H	178-179	-	-	+	++		
150	S	Me	DTI	H		-	-	-			++1
151	S	4-CNØ	DTI	H	186	-	+	+++5		-	+++7
152	S	4-MeØ	DTI	H	181	-	-	+1		-	+++3
153	S	4-FØ	DTI	H	180	+1	+1	+3		-	+++7
154	S	4-t-BuØ	DTI	H	120	+1	+1	+1		-	+++1
155	S	4-ClØ	DTI	H		-	-	++		-	+++1
156	S	Ø	DTI	H		-	-	++		+	+++3
157	S	4-BrØ	DTI	H		-	-	+++5		++	++
158	S	4-MeOØ	DTI	H		-1	+1	+3		-1	+++1
159	S	3,4- Cl ₂ Ø	DTI	H		-1	-1	++1		-1	+++1
160	S	4-CF ₃ Ø	DTI	H		-	-	+++6		-1	+++1
161	O	4-ClØ	DTI	H	195-196						
162	S	C ₈ H ₁₇ S	DTI	H							
163	S	BzS	DTI	H							
164	S	EtS	DTI	H							

Table 7



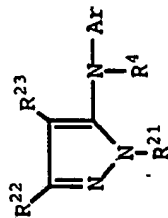
Compound	R ²⁰	Ar	R ⁴	melting point °C	POWD MDEW	RICE BLAST	LEAF RUST	DOWN MDEW SQUASH	LEAF BLOT	DOWN MDEW GRAPE
165	Ø	DTI	H		+1	+1	+++5		+1	+++9
166	4-ClØ	DTI	H		+1	+1	+++7		+	+++1
167	4-MeØ	DTI	H		-1	-1	+1		-1	+++3
168	3,4- Cl ₂ Ø	DTI	H		+1	+1	+++6		-1	+++3
169	4-t-BuØ	DTI	H		+1	++1	++3		+++1	+++1
170	3-ClØ	DTI	H							
171	4-FØ	DTI	H							
173	4-BrØ	DTI	H							
173	4-MeØ	DTI	H							
174	4-CF ₃ Ø	DTI	H							
175	4-CNØ	DTI	H							
176		DTI	H							
177		DTI	H							
178	4-NMe ₂ Ø	DTI	H							

Table 8A



Compound	R ²¹	R ²²	R ²³	Ar	R ⁴	melting point °C	POWD MDEW	RICE BLAST	LEAF RUST	DOWN MDEW SQUASH	LEAF BLOT	DOWN MDEW GRAPE
179	Me	Me	H	DTI	H	167.2	-	-	-		-	-
180	Me	t-Bu	H	DTI	H	88-95	++	+	++		-	++
181	Me	t-Bu	H	o-DTI	H							
182	Ø	Ø	H	DTI	H							
183	3-CF ₃ Ø	H	CN	DTI	H	154-155	-1 2G	-1 2G	+++2 2G		-1 2G	+++1 3G
184	4- CF ₃ ØØ	H	CN	DTI	H	111-112.5	++1 2G	+1	+++8 2G		+++ 2G	+++ 2G
185	2- pyridyl	Ø	H	DTI	H							

Table 8B

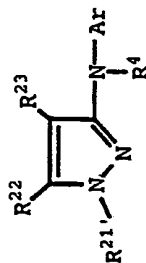


Compound	R21	R22	R23	Ar	R4	melting point °C	POWD MDEW	RICE BLAST	LEAF RUST	DOWN MDEW SQUASH	LEAF BLOT	DOWN MDEW GRAPE
267	4-MeO	H	CN	DTI	H	134-136						
268	4-Cl	H	CN	DTI	H	179-182						
269	3-Cl	H	CN	DTI	H	155-158						
270	2-Cl	H	CN	DTI	H	158-160						
271	2,4- Cl2	H	CN	DTI	H	164-166						
272	2-CF3	H	CN	DTI	H	171-173						
273	Ø	H	4- NO2 SO2	DTI	H	89-90						
274	3-NO2	H	4-Cl	DTI	H	205-206						
275	Ø	H	4- CN	DTI	H	175-176						
276	3-NO2	H	3-Cl	DTI	H	178-179						
277	Ø	H	4- FOSO2	DTI	H	83-85						
278	Ø	Ø	Br	DTI	H	96-97						
279	Me	Me	CN	DTI	H	153-155						
280	3-Me	H	CN	DTI	H	148-150						
281	3-Br	H	CN	DTI	H	134-136						
282	Me	t-Bu	H	DTI	H	134-136						
283	4- CF3	H	CN	o-DTI	H	158-160	-	-	+		-	+

Compound	R ²¹	R ²²	R ²³	Ar	R ⁴	melting point °C	POWD MDEW	RICE BLAST	LEAF RUST	DOWN MDEW SQUASH	LEAF BLOT	DOWN MDEW GRAPE
284	Me	t-Bu	Br	DTI	H	178-180	+	-		-	-	+++1 1
285	t-Bu	H	CN	DTI	H	112-114	+++1 62G	+++1 53G			-	+++2 84G
286	Ø	Ø	H	DTI	H	70 dec	-1 1	-1 1			-1 1	+++1 7
287	CF ₃ CH ₂	H	CN	DTI	H	144-146	+++6 92G	-1 04G	++		-1 12G	+++8 93G
288	Me	H	CN	DTI	H	173-175	-1 4	-1 1			-1 1	+++6 7
289	4-Me MeOSO ₂	H	CN	DTI	H	179-181	-1 1	-1 1	-		-1 1	+++1 3
290	t-Bu	H	CN	4-(C ₂ F ₅) -2,6-(NO ₂) ₂ -Ø	H	124-125	+++3 92G	+++1 1	++		+1 1	+++1 93G
291	3-NO ₂ Ø	H	Ø	DTI	H	71-75	+1 1	+1 3	++		+++1 7	+++8 9
292	Ø	H	CN	DTI	H	164-166	-1 1	-1 1	-		-1 1	+++3 92G
293	Ø	H	4-ClØ	DTI	H	76-78 (d)	-1 1	+1 4	++		+++1 7	+++1 6
294	Ø	H	3-CF ₃ Ø	DTI	H	157-158	-1 1	-1 1	+		-1 1	-1 1
295	Ø	H	4-MeØ	DTI	H	120-121	+++1 1	-1 1	+		-1 1	-1 1
296	Ø	H	3-ClØ	DTI	H	145-147	-1 1	-1 1	+		-1 1	+++1 7
297	4-CF ₃ Ø	H	CN	3-Cl DTI	H	90-92	+1 1	+1 1	++		-1 1	+++1 3
298	Ø	H	EtOOC-	DTI	H	119-120	-1 1	-1 1	++		+++1 8	+++3 9

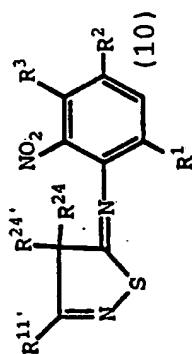
Compound	R21	R22	R23	Ar	R4	melting point °C	POWD MDEW	RICE BLAST	LEAF RUST	DOWN MDEW SQUASH	LEAF BLOT	DOWN MDEW GRAPE
299	Me	Me	Br	DTI	H							
300	4-FØ	H	CN	DTI	H	162-165						
301	4-FØ	H	CN	DTI	Na	255-256						
302	3-ClØ	H	3-CF3Ø	DTI	H	179-180						
303	3-ClØ	H	4-MeØ	DTI	H	107-109						
304	3-ClØ	H	4-ClØ	DTI	H	174-175						
305	Ø	H	BzOOC-	DTI	H	125-126						
306	Me	H	Ø	DTI	H	204-205						
307	3-ClØ	H	3-ClØ	DTI	H							
308	3-ClØ	H	Ø	DTI	H	154-155						
309	Ø	H	iPrOOC	DTI	H	133-134						
310	Ø	H	nBuOOC	DTI	H							
311	Ø	H	2-Me- PrOOC-	DTI	H							

Table 8C



Compound	R ^{21'}	R ²²	R ²³	Ar	R ⁴	melting point °C	POWD MDEW	RICE BLAST	LEAF RUST	DOWN MDEW SQUASH	LEAF BLOT	DOWN MDEW GRAPE
312	t-Bu	Me	CN	DTI	H	118-121						
313	Me	Me	CN	DTI	H	153-155						

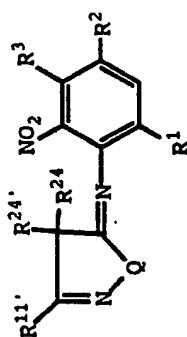
Table 9A



Compound	R ²⁴	R ^{24'}	R ^{11'}	R ¹	R ²	R ³	MP °C	POWD MDEW	RICE BLAST	SQUASH			LEAF RUST	DOWN MDEW	LEAF BLOT	DOWN MDEW	GRAPE
186	Cl	Cl	Me	CF ₃	NO ₂	H	143-145.5	-	-	+++8	+++9 2G						
187	Cl	Cl	4-FØ	CF ₃	NO ₂	H	155-157	-	-	++	+						
188	Br	Cl	Et	CF ₃	NO ₂	H	116-120	+++1 2G	-	+++8 2G	+++9 3G						
189	Br	Cl	Me	CF ₃	NO ₂	H	145-149	+++1 3G	+	+++6 2G	+++6 3G						
190	Cl	Cl	n-Bu	CF ₃	NO ₂	H	114-115	+++6	-	+++8	+++6						
191	Br	Br	Me	CF ₃	NO ₂	H	148-151	+++1 2G	-	+++7	+++7						
192	Br	Cl	Me	NO ₂	CF ₃	H	133-137	+++3 2G	+++4 2G	+++6 2G	+++8						
193	Cl	Cl	1-Et-1-MePr	NO ₂	CF ₃	H	143-145	+++3	+	+++6	+++7						
194	Cl	Cl	n-Bu	NO ₂	CF ₃	H	115-128	+++6	++5	+++8	+++7						
195	Cl	Cl	Me	NO ₂	CF ₃	H	130-134	+++3 2G	+	+++7 2G	+++6 2G	+++6 2G	+++6 2G	+++8			
196	Cl	Cl	t-Bu	NO ₂	CF ₃	H	157-159	+++6	+++8	+++8	+++6	+++6	+++1				
197	Br	Br	Me	NO ₂	CF ₃	Cl	143-145	-	++1	+++3			+++4	+++1 4G			
198	Cl	Cl	Me	NO ₂	CF ₃	Cl	130-134	+	+++1	+++4			+++1	+++7			
199	Cl	Cl	-CH ₂ -C ₆ H ₁₁	NO ₂	CF ₃	H	138-143	-1	++1	+++5			+++1	+++1	+++1		
200	Cl	Cl	i-Pr	NO ₂	CF ₃	H	130-133	+++1 2G	++1	+++5 2G			+++1 2G	+++1 2G	+++1		

Compound	R24	R24'	R11'	R1	R2	R3	MP °C	POWD MDEW	RICE BLAST	LEAF RUST	DOWN MDEW SQUASH	LEAF BLOT	DOWN MDEW GRAPE
201	Cl	Cl	4-ClØ	NO2	CF3	H	220-222	++1	+1	+++6		++1	++
202	Cl	Cl	4-FØ	NO2	CF3	H	180-182	++1	++1	++1		+++1	+++6
203	Cl	Cl	i-Pr	CF3	NO2	H		+++1 3G	+++1 2G	+++8 3G		-1 3G	+++3 5G
204	Br	Br	Me	NO2	t-Bu	H	171-173	-	-	-		-	-
205	Cl	Cl	Me	NO2	t-Bu	H	179-181	-	-	-		-	-
206	Br	Br	Me	t-Bu	NO2	H	141-143.5	-	+	+++7 2G		-	+++9 4G
207	Cl	Cl	Me	t-Bu	NO2	H	136-137	++1	+	+++1		+	+++8 4G

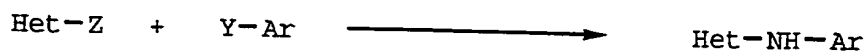
Table 9B



Compound	Q	R24	R24'	R11'	R1	R2	R3	MP °C	POWD MDEW	RICE BLAST	LEAF RUST	SQUASH		LEAF BLOT	DOWN MDEW	GRAPE MDEW
314	O	Cl	Cl	1-Et-1-MePr	NO2	CF3	H	114- 115								
315	O	Cl	Cl	t-Bu	NO2	CF3	H	135- 136								
316	S	Cl	Cl	t-Bu	CF3	NO2	H	132- 133	+++1 73G	+++1 83G	+++8 93G			++1 13G	+++33G 05G	

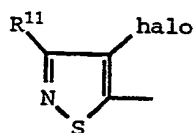
Synthesis

Compounds of general formula (1) wherein R¹ is H or halo can be prepared using the following general procedure:

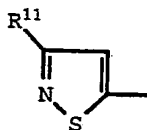


- 5 wherein one of Y and Z is NH₂ and the other is halo. The reaction is preferably carried out in the presence of a base such as an alkali metal hydroxide, carbonate, hydride or alkaline earth metal hydroxide or carbonate. Preferred bases are sodium hydride, sodium hydroxide, sodium carbonate, potassium carbonate, potassium t-butoxide, sodium bicarbonate and potassium hydroxide. The reaction is carried out in a nonreactive organic solvent such as tetrahydrofuran, at a temperature in the range from -20 to 200°C. It is preferred for Y to be halo and Z to be NH₂.

- 15 Compounds of formula (1) wherein Het is



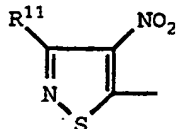
- can be synthesized by the foregoing general procedure, using a 4-halo-5-isothiazolamine starting material. Alternatively, they can be prepared by halogenating a compound of formula (1) wherein Het is



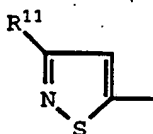
- Halogenation is typically carried out by reacting the compound of formula (1) with a small excess of elemental bromine, chlorine, or iodine in CH₂Cl₂ or CHCl₃. Bromination and chlorination usually proceed rapidly at room temperature. Iodination may require addition of potassium carbonate or sodium carbonate and brief heating to reflux. Other

halogenating agents, such as N-bromosuccinimide and N-chlorosuccinimide may also be used.

Compounds of formula (1) wherein Het is

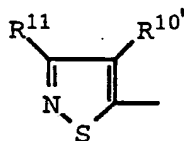


5 can be made by nitrating a compound of formula (1) wherein Het is



Nitration is typically carried out by dissolving the compound of formula (1) in concentrated sulfuric acid and adding excess
10 fuming nitric acid at room temperature. If no conversion has occurred within ten minutes, brief heating at 100°C may be used.

Compounds of formula (10) are prepared by halogenating a compound of formula (1) wherein Het is

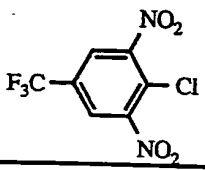
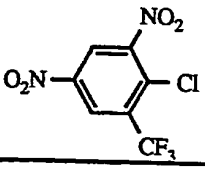
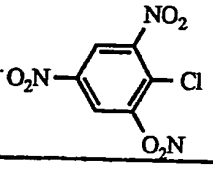
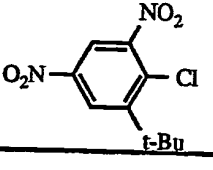
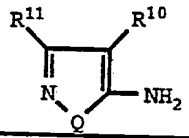
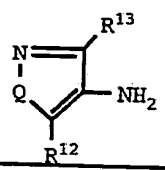
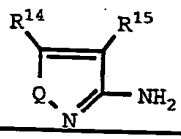


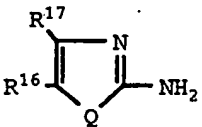
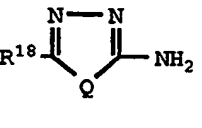
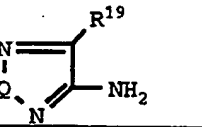
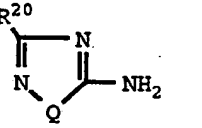
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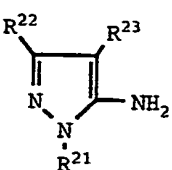
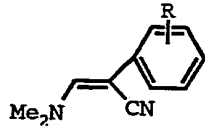
wherein R^{10'} is H or halo.

Starting Materials

The starting materials used in preparing compounds of the invention are commercially available or they are readily
20 prepared by known synthetic methods. The following table identifies some of the available sources for the starting materials.

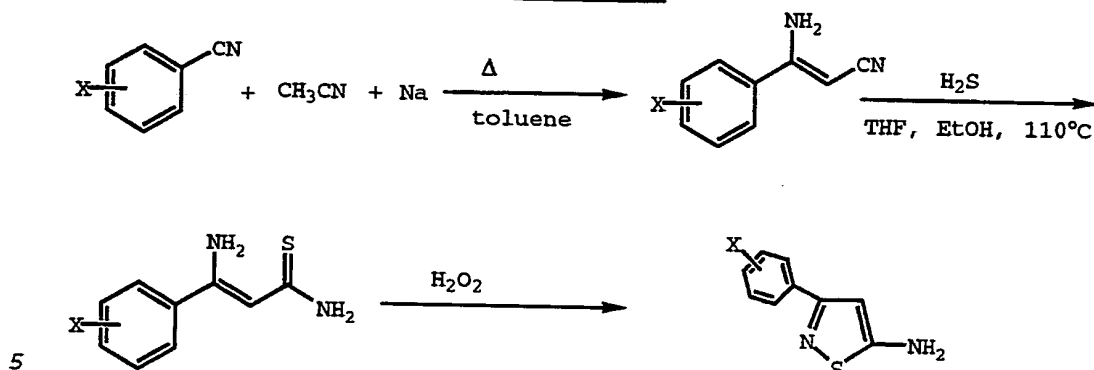
Starting Material	Source
	commercially available
	commercially available
	commercially available
	Preparation 1
	J. Het. Chem, 26, 1575 (1989); J. Med. Chem, 18,441 (1975) GB Patent 1,226,913
	Ann. Chem., 1543 (1979); J. Het. Chem, 24, 243 (1987)
	J. Het. Chem, 26, 1575 (1989)

	<p>J. Het. Chem 28, 1003 (1991); J. Het. Chem. 28, 1017 (1991); JACS, p. 2242 (1945); JACS, p. 871 (1946); JACS 72, p. 3722 (1950); JACS 75, p. 4057 (1953); JACS 64, p. 2902 (1942); J. Ind. Chem Soc 30, p. 398 (1953); Ber Deutsch Chem Ges 92, p. 22 (1959); J. Ind. Chem. Soc. 36, p. 434 (1959); J Prakt Chem, 312, p. 359, (1970); Chem Pharm Bull, 10, p. 376 (1962); Ber Deutsch Chem Ges 99, p. 2110 (1966); Zh. Org. Khim. 16(10), p. 2185 (1980)</p>
	<p>J. Chem. Soc. Perkin Trans. I 1918 (1972); J. Chem. Soc. Perkin Trans. I 1718 (1972); J. Indian Chem. Soc., 59, 277 (1982); Indian J. of Chem. 24B, 1154 (1985); J. Het. Chem. 17, 607 (1980); J. Het. Chem. 14, 853 (1977); Synth. Meth. 18, p. 305; Synth Meth. 27, p. 501</p>
	<p>U. S. Patent 4,555,521</p>
	<p>Ber. Deutsch Chem. Ges., 87, p.57 (1954); Ber. Deutsch Chem. Ges., 89, p.2742 (1956); Ber. Deutsch Chem. Ges., 93, p.397 (1960); Bull. Chem. Soc. Jpn., 46, 1765 (1973)</p>

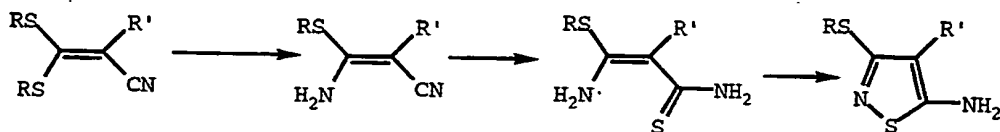
	<p>Heterocycles, v. 23(2), p365 (1985); Heterocycles, v. 26(3), pp 613-616 (1987); J. Indian Chem Soc. 64(6), 345-7 (1987); Helv. Chim. Acta, 41, p. 306 (1958); Zh Org Khim, 1, p. 1341, (1965); Org Synth, 48, p. 8 (1968); Indian J. Chem. 28B, 346-48 (1989); J. Med. Chem. v. 27(11) p. 1396; JAMCS v. 81, p 2456 (1959), US Patent 4,980,472; Aust. J. Chem. v. 44(9), 1263-67 (1991)</p>
	<p>Tetrahedron, vol. 28 (9), pp. 2377-81 (1972); Tetrahedron, vol 24 (6), pp. 2481-84 (1968)</p>

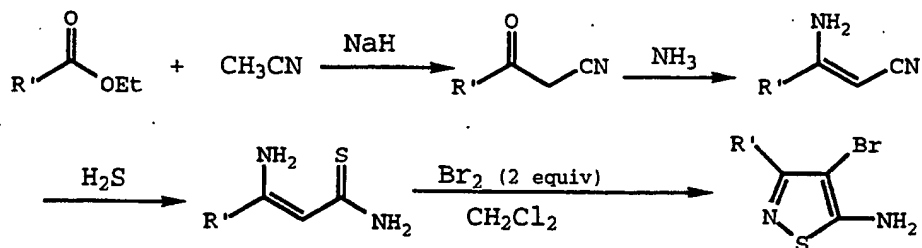
For example, 5-aminoisothiazole starting materials can be prepared by the routes illustrated in the following Schemes 1A-1C:

Scheme 1A



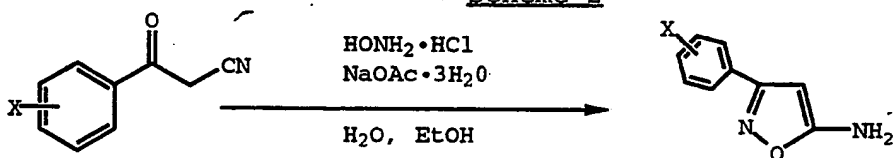
Scheme 1B



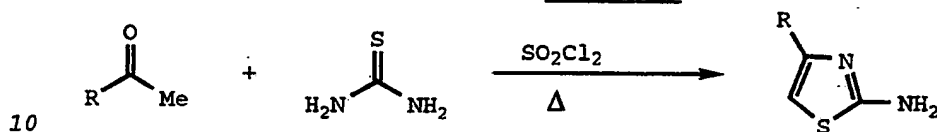
Scheme 1C

5-Aminoisoxazole starting materials can be prepared, for example, by the procedure illustrated in Scheme 2.

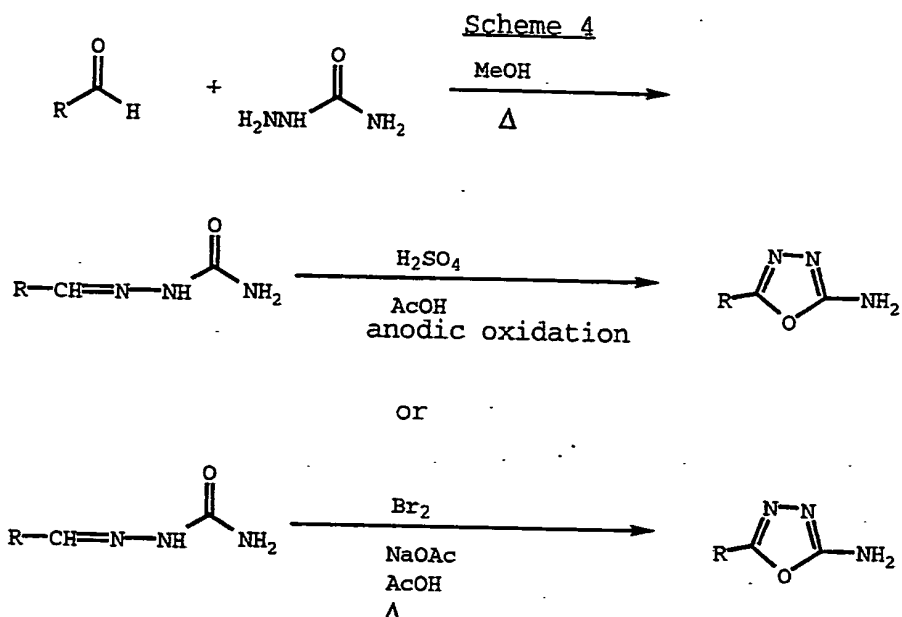
5

Scheme 2

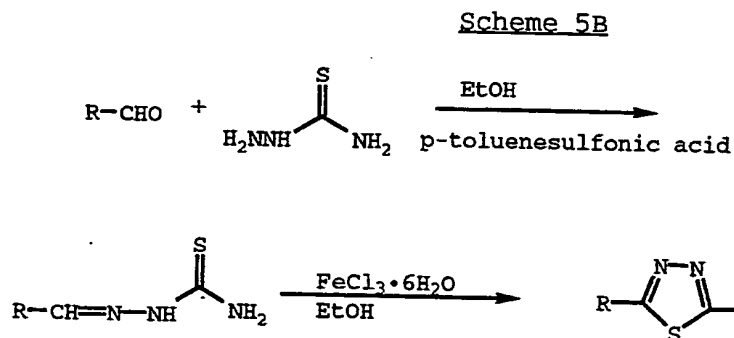
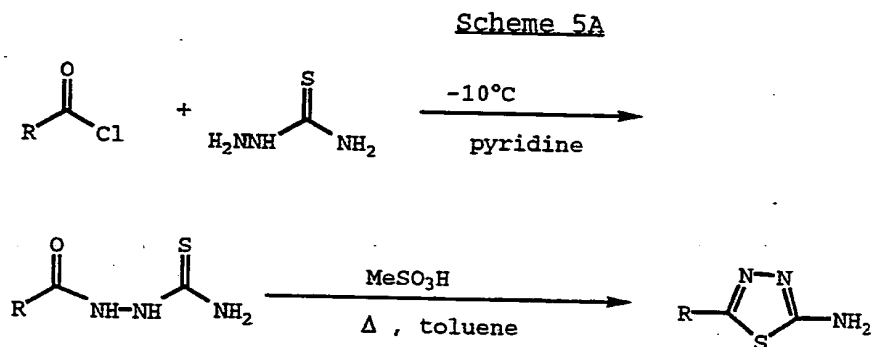
2-Aminothiazole starting materials can be prepared, for example, by the procedure illustrated in Scheme 3.

Scheme 3

2-Amino-1,3,4-oxadiazole starting materials can be prepared, for example, by the procedure illustrated in Scheme 4.

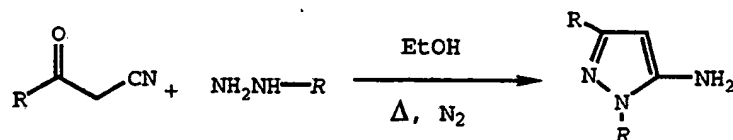


2-Amino-1,3,4-thiadiazole starting materials can be prepared, for example, by the procedure illustrated in Schemes 5A and 5B



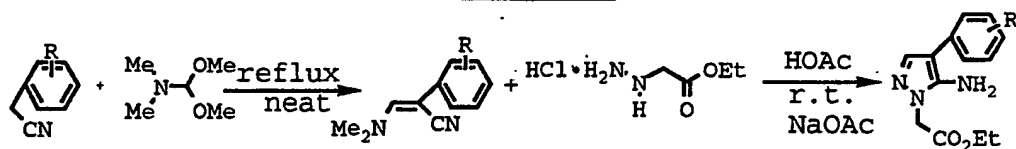
5-Aminopyrazole starting materials can be prepared, for example, by the procedures illustrated in Scheme 6A-6D.

Scheme 6A

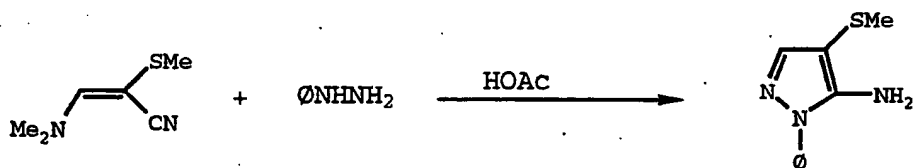


5

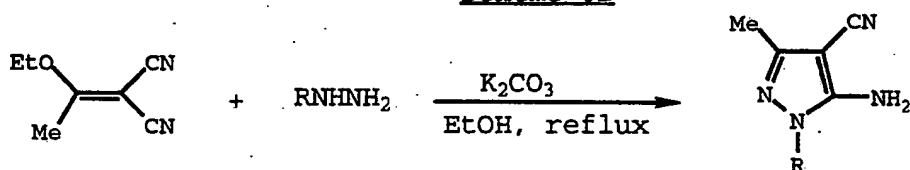
Scheme 6B



Scheme 6C

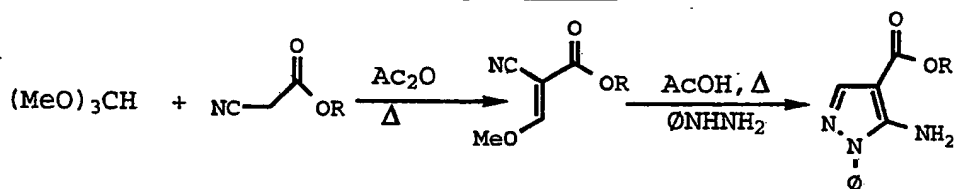


Scheme 6D

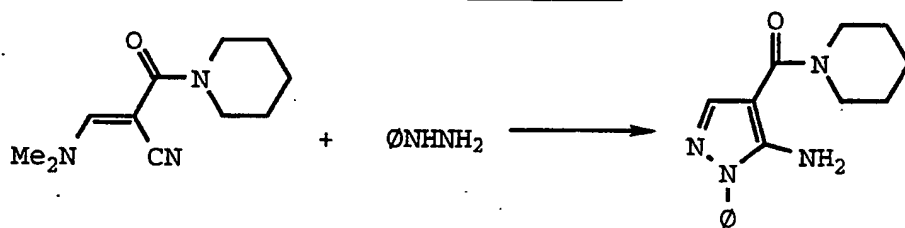


10

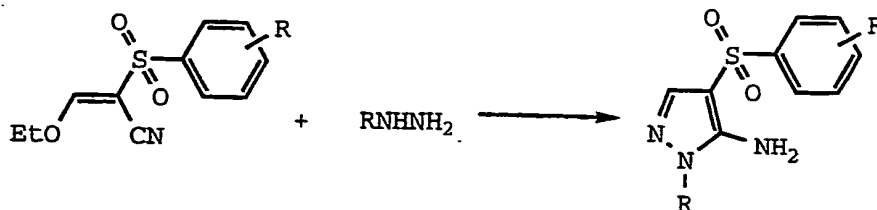
Scheme 6E



Scheme 6F

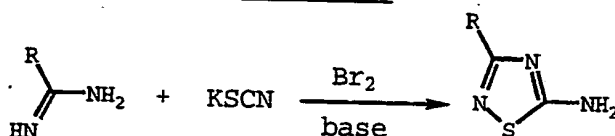


Scheme 6G

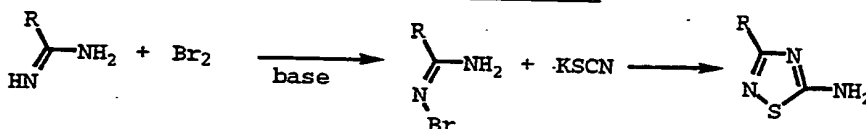


5-Amino-1,2,4-thiadiazole starting materials can be prepared, for example, by the procedures illustrated in Schemes 7A and 7B.

Scheme 7A



Scheme 7B



Preparation 1

2-t-Butyl-4,6-dinitrochlorobenzene

To mechanically stirred concentrated nitric acid (750mL), cooled to 0°C, was added 150.2 g (1 mole) of 2-t-butylphenol at such a rate that the reaction temperature never exceeded 10°C. The mixture was stirred one-half hour after the addition of the phenol was completed. Then the mixture was poured upon ice in a 4L beaker and allowed to stand overnight at room temperature. After filtering the mixture, the precipitate was washed with water and recrystallized from 800 mL of ethanol and cooled in a refrigerator. 2-t-Butyl-4,6-dinitrophenol, in the form of yellow prisms, was collected by suction filtration and air dried. Yield 84.0 g. M.P. 125-128°C.

To a suspension of 60.01 g (0.25 mole) of 2-t-butyl-4,6-dinitrophenol in 125 mL of 1,2-dichloroethane was added 38.3 g (0.275 mole) of 2,4,6-trimethylpyridine. Mechanical stirring was started and 115 g (0.75 mole) of phosphorous oxychloride

was added in many small portions, keeping the temperature of the mixture below 50°C. The mixture was then stirred for 40 hours under reflux. The cooled mixture was then poured into hot water (55°C) a little at a time. Ice was added whenever
5 the reaction temperature exceeded 65°C. The mixture was extracted with 1L of CHCl₃ and again with 500 mL of CHCl₃. The combined extracts were washed twice with water and dried over anhydrous Na₂SO₄ and filtered. The filtrate was concentrated in a rotary evaporator to a black oil that
10 crystallized on standing. The solid was dissolved in 1L of benzene, treated with 100 g of florisil and filtered. The filtrate was concentrated to a wine colored oil, which was dissolved in 200 mL of Skelly B and chilled. White platelets of the title product formed. Yield 59.2 g. M.P. 62-63°C.

15

Preparation 2

5-amino-4-bromo-3-ethylisothiazole

Sodium hydride (60%, 32.0 g, 0.8 mole) was suspended in dry THF (250 mL) and heated to reflux (70°C) with vigorous stirring. To this suspension was added a mixture of ethyl
20 propionate (30.7 g, 0.3 mole) and acetonitrile (27.0 g, 0.6 mole) over a 2.0 hour period and further refluxed for 9.0 hours. After cooling to 25°C, ethanol (15.0 mL) followed by water (350 mL) was added to the reaction mixture. To the resulting yellowish-brown solution was added hexane (500 mL)
25 and vigorously stirred. The aqueous layer obtained was washed with hexane/ethyl ether (2:1, 400 mL), acidified with 5N HCl (about 130 mL) and then extracted with dichloromethane. The combined organic extracts were dried over sodium sulfate, filtered and concentrated to give 28.0 g of 3-oxopentane
30 nitrile (96%).

Ammonia (about 3.5 g) was bubbled at a steady rate over a 5.0 min period through a solution of 3-oxopentane nitrile (7.09, 72.2 mmol) in absolute ethanol (130 mL) in a heavy wall tube (Ace Glass Inc.) and immediately sealed with a
35 teflon plug. The sealed tube was then placed in an oven and heated at 110°C for 16 hours. After cooling to 2°C, the

solvent was removed under vacuum to give 6.39 of 3-aminopentene nitrile (91%) as red oil.

5 H₂S (7.2 g) was bubbled at a steady rate over a 4.5 min period through a solution of 3-aminopentene nitrile (11.1 g, 115.6 mmol) in THF (35 mL) and ethyl alcohol (25 mL) at 0°C in a heavy wall tube and immediately sealed with a teflon plug. After the reaction mixture was allowed to warm to 25°C, the sealed tube was placed in an oven and heated 90°C for 3 hours. The sealed tube was allowed to stand at 25°C for 48.0 hours
10 and then removal of solvent under vacuum gave 3-amino-2-pentene thioamide 14.5 g of 1b (96% yield) as thick red oil.

Bromine (2.72g, 17.0 mmol) in dichloromethane (50.0 mL) was added dropwise to a solution of 3-amino-2-pentene thioamide (1.1g, 8.5 mmol), in dichloromethane (50.0 mL) at
15 5°C over a 30 min period. The resulting reddish-brown solution was stirred at ambient temperature for 2 hours. After the removal of dichloromethane in vacuo, the residue was titrated with ethyl acetate. The white solid obtained was filtered to give and basified, pH between 9 to 10, with
20 ammonium hydroxide and extracted with dichloromethane. The combined organic extracts were dried over sodium sulfate, filtered and concentrated to give 5-amino-4-bromo-3-ethylisothiazole (1.30g, 74%) as a yellow oil.

Example 1

25 3-methyl-N-[2,6-dinitro-4-(trifluoromethyl)phenyl]isothiazol-5-amine

To a solution of 1.14 g (.01 mole) of 3-methylisothiazol-5-amine and 2.78 g (.01 mole) of 4-chloro-3,5-dinitrobenzotrifluoride in about 50 mL of anhydrous THF was
30 added 0.7 g of 50% NaH in oil. On the following day TLC showed some starting material remained. A few milliliters of ethyl alcohol were added and the mixture was evaporated to dryness under vacuum providing a black solid. This residue was boiled up in hexane. The resulting black red material was
35 isolated by decanting the hexane and the residue was dissolved in water. When the aqueous mixture was acidified a dark

orange oil formed, which was extracted into methylene chloride. The extract was filtered and concentrated to dryness under vacuum. The resulting material was first purified by chromatography ($\text{SiO}_2/3:1 \text{ Et}_2\text{O}/\text{Pentane}$) then recrystallized in
5 hexane, providing 1.1 g of yellow-orange crystalline powder. M.P. 118-120°C.

Example 2

4-bromo-3-methyl-N-[2,6-dinitro-4-(trifluoromethyl)-phenyl]isothiazol-5-amine

10 To a solution of 0.9 g (.0025 mole) of 3-methyl-N-[2,6-dinitro-4-(trifluoromethyl)phenyl]isothiazol-5-amine in about 50 mL of CHCl_3 was added 0.46 g of Br_2 with swirling. The solution became cloudy and then turned clear orange. The solution was washed with water, filtered, and evaporated to
15 dryness under vacuum to provide 1.14 g of a bright yellow solid. The product was again washed with water, filtered, and dried, providing 0.98 g of golden-yellow crystals. M.P. 171-172°C.

Example 3

20 N-(4-bromo-3-methylisothiazol-5-yl)-N-[2,6-dinitro-4-(trifluoromethyl)phenyl]acetamide

To a solution of 0.64 g of 4-bromo-3-methyl-N-[2,6-dinitro-4-(trifluoromethyl)phenyl]-5-isothiazolamine in about 15 mL of acetic anhydride was added about 1 g of granular
25 K_2CO_3 . The mixture was heated to near reflux temperature for about 1 minute. The solution was then filtered and the salts were washed with ethyl ether. The solution was concentrated to dryness under vacuum providing a dark oil, which was equilibrated between ethyl ether and dilute HCl . Hexane was
30 added to the mixture, the aqueous layer was removed, and the organic layer was concentrated under vacuum to provide .72 g of orange oil. Crystallization from $\text{Et}_2\text{O}/\text{hexane}$ provided yellow-brown crystals. Recrystallization from $\text{CH}_2\text{Cl}_2/\text{hexane}$ provided .55 g of the title product. MP 136-139°C.

Example 4

3-methyl-4-nitro-N-[2,6-dinitro-4-(trifluoromethyl)-phenyl]isothiazol-5-amine

A solution of 0.5 g of 3-methyl-N-[2,6-dinitro-4-(trifluoromethyl)phenyl]isothiazol-5-amine in 10 mL of concentrated sulfuric acid was warmed to 50°C on a steam bath. To this solution was added 2 mL of fuming nitric acid. After swirling, the mixture was allowed to stand for 10 minutes. The mixture was first diluted with ice water, then flooded with 150 mL of water. The resulting yellow powder was isolated by filtration and air dried to provide 0.89 g of product, which was purified by recrystallization from CHCl₃/hexane to provide 0.66 g of the title product. MP 175-178°C.

Example 5

3-ethyl-4-bromo-N-[2,6-dinitro-4-(trifluoromethyl)phenyl]isothiazol-5-amine

To a solution of 0.45 g of 4-bromo-3-ethylisothiazol-5-amine and 0.6 g of 4-chloro-3,5-dinitro-benzotrifluoride in 75 mL of anhydrous THF was added 0.25 g of 50% NaH in oil. On the following day, TLC showed some starting material remained. Two milliliters of ethyl alcohol were added and the mixture was concentrated to dryness under vacuum providing a black solid. This residue was dissolved in water. When the aqueous mixture was acidified with dilute HCl the solution turned a bright yellow. An extraction using hexane/Et₂O was followed by extractions using dilute sodium hydroxide until the organic layer showed only a single product when tested using TLC. The aqueous layer was separated, acidified, and extracted with hexane/Et₂O to provide a material which was recrystallized from pentane to provide 0.5 g of the title product. MP 99-103°C.

Example 6

N-(4-bromo-4-chloro-3-methyl-5(4H)-isothiazolylidene)-
2,4-dinitro-6-(trifluoromethyl)benzenamine

Excess chlorine was bubbled into a solution of 0.56 g of
5 4-bromo-3-methyl-N-[2,6-dinitro-4-(trifluoromethyl)-
phenyl]isothiazol-5-amine in 50 mL of chloroform. After ten
minutes the solution was concentrated to dryness under vacuum
to provide 0.52 g of the title product as a yellow solid.
Recrystallization from hexane gave pale yellow crystals. MP
10 133-137°C.

Example 7

N-(4,4-dichloro-3-n-butyl-5(4H)-isothiazolylidene)-2,4-
dinitro-6-(trifluoromethyl)benzenamine

A solution of 0.65 g of 3-n-butyl-N-[2,6-dinitro-4-
15 (trifluoromethyl)phenyl]isothiazol-5-amine in 30 mL of
chloroform was saturated with chlorine. After 3 to 4 minutes
TLC indicated that the reaction had progressed to completion.
The mixture was concentrated under vacuum to provide 0.82 g of
a clear yellow oil. The oil was dissolved in pentane and
20 crystals slowly developed. After cooling the mixture in a
freezer, 0.43 g of pale orange crystals were collected. MP
115-120°C.

Example 8

3,N-Dimethyl-N-[2,6-dinitro-4-
25 (trifluoromethyl)phenyl]isothiazol-5-amine

To 3-methyl-N-[2,6-dinitro-4-(trifluoromethyl)-
phenyl]isothiazol-5-amine (1.4 g, .004 mole) in 75 mL of
methylethyl ketone was added 3 g of potassium carbonate and 2
g of methyl iodide. The container was stoppered and stirred
30 for 48 hours. The mixture was filtered, then the organic
layer was concentrated using a rotary evaporator to give 1.3 g
of a red solid, which was purified on a SiO₂/CHCl₃ column,
then recrystallized from hexane. Yield .27g. M.P. 147-149°C.

The compounds of the present invention have been found to
35 control fungi, particularly plant pathogens. When employed in
the treatment of plant fungal diseases, the compounds are

applied to the plants in a disease inhibiting and phytologically acceptable amount. The term "disease inhibiting and phytologically acceptable amount," as used herein, refers to an amount of a compound of the invention which kills or inhibits the plant disease for which control is desired, but is not significantly toxic to the plant. This amount will generally be from about 1 to 1000 ppm, with 10 to 500 ppm being preferred. The exact concentration of compound required varies with the fungal disease to be controlled, the type formulation employed, the method of application, the particular plant species, climate conditions and the like. A suitable application rate is typically in the range from .25 to 4 lb/A. The compounds of the invention may also be used to protect stored grain and other non-plant loci from fungal infestation.

Greenhouse Tests

The following screen was used to evaluate the efficacy of the present compounds against a variety of different organisms that cause plant diseases.

The test compounds were formulated for application by dissolving 50 mg of the compound into 1.25 ml of solvent. The solvent was prepared by mixing 50 ml of "Tween 20" (polyoxyethylene (20) sorbitan monolaurate emulsifier) with 475 ml of acetone and 475 ml of ethanol. The solvent/compound solution was diluted to 125 ml with deionized water. The resulting formulation contains 400 ppm test chemical. Lower concentrations were obtained by serial dilution with the solvent-surfactant mixture.

The formulated test compounds were applied by foliar spray. The following plant pathogens and their corresponding plants were employed.

Pathogen	Designation in Tables 1-9	Host
<i>Erysiphe graminis tritici</i> (powdery mildew)	POWD MDEW	wheat
<i>Pyricularia oryzae</i> (rice blast)	RICE BLAST	rice
<i>Puccinia recondita tritici</i> (leaf rust)	LEAF RUST	wheat
<i>Septoria nodorum</i> (glume blotch)	LEAF BLOT	wheat
<i>Plasmopara viticola</i> (downy mildew)	DOWN MDEW	grape

The formulated technical compounds were sprayed on all foliar surfaces of the host plant (or cut berry) to past run-off. Single pots of each host plant were placed on
5 raised, revolving pedestals in a fume hood. Test solutions were sprayed on all foliar surfaces. All treatments were allowed to dry and the plants were inoculated with the appropriate pathogens within 2-4 hours.

Tables 1-9 report the activity of typical compounds of
10 the present invention when evaluated in this experiment. The effectiveness of test compounds in controlling disease was rated using the following scale.

0	=	not tested against specific organism
-	=	0-19% control at 400 ppm
15	+	20-89% control at 400 ppm
	++	90-100% control at 400 ppm
	+++	90-100% control at 100 ppm

An arabic numeral following this rating gives the control rating at 6.25 ppm on the following scale:

rating	disease control
1	0-19%
2	20-29%
3	30-39%
4	40-59%
5	60-74%
6	75-89%
7	90-96%
8	97-99%
9	100%

Phytotoxic effects, if any, observed when the compound was tested at 100 ppm are also reported in the line below the activity rating in Tables 1-9. This rating consists of an arabic numeral and a letter. The arabic numeral reports the degree of chemical injury as rated on the following scale:

rating	degree of injury
1	none
2	slight
3	moderate
4	severe
5	death

The letter reports the type of symptomology observed, using the following code:

letter	symptom
S	stunting
C	chlorosis
G	general necrosis
F	formative
W	wilting

Insecticide and Miticide Utility

10 The compounds of formulas (1) and (10) show activity against a number of insects and mites.

The compounds of formulas (1) and (10) are useful for reducing populations of insects and mites, and are used in a method of inhibiting an insect or mite population which
15 comprises applying to a locus of the insect or mite an effective insect- or mite-inactivating amount of a compound of formulas (1) and (10). The "locus" of insects or mites is a term used herein to refer to the environment in which the insects or mites live or where their eggs are present,

including the air surrounding them, the food they eat, or objects which they contact. For example, plant-ingesting insects or mites can be controlled by applying the active compound to plant parts, which the insects or mites eat, particularly the foliage. It is contemplated that the compounds might also be useful to protect textiles, paper, stored grain, or seeds by applying an active compound to such substance. The term "inhibiting an insect or mite" refers to a decrease in the numbers of living insects or mites; or a decrease in the number of viable insect or mite eggs. The extent of reduction accomplished by a compound depends, of course, upon the application rate of the compound, the particular compound used, and the target insect or mite species. At least an insect-inactivating or mite-inactivating amount should be used. The terms "insect-inactivating amount" and "mite-inactivating amount" are used to describe the amount, which is sufficient to cause a measurable reduction in the treated insect or mite population. Generally an amount in the range from about 1 to about 1000 ppm active compound is used.

In a preferred embodiment, the present invention is directed to a method for inhibiting a mite which comprises applying to a plant an effective mite-inactivating amount of a compound of formulas (1) and (10) in accordance with the present invention.

MITE/INSECT SCREEN

The compounds of the foregoing examples were tested for miticidal and insecticidal activity in the following mite/insect screen.

Each test compound was formulated as a 400 ppm solution, and this solution was then diluted with water to give the indicated concentrations. The 400 ppm solution was prepared by combining 19.2 mL of .05% solution

of Tween 20 (polyoxyethylene (20) sorbitan monolaurate) in water with a solution of 8 mg of the compound in .8 mL of acetone/EtOH (9/1).

Twospotted spider mites (*Tetranychus urticae* Koch) and
5 melon aphids (*Aphis gossypii* Glover) are introduced on squash cotyledons and allowed to establish on both leaf surfaces. Other plants in the same treatment pot are left uninfested. The leaves are then sprayed with test solution using an atomizing sprayer at 17 psi. Both surfaces of the leaves are
10 covered until runoff, and then allowed to dry. Activity of a compound is determined 48 hours after treatment. Activity is rated as a percent based on the mites/aphids present in plants sprayed with solvent alone. An uninfested plant is cut after the spraying and drying steps and placed into a Petri dish
15 containing larval southern armyworm (*Spodopetra eridania* Cramer). The larvae are checked after 72 to 96 hours for mortality and for antifeedent activity of the compound. The ratings are based on comparison to results on plants sprayed with solvent alone.

20 Activity on Southern corn rootworm (*Diabrotica undecimpunctata howardi* Barber) is evaluated by adding one mL of test solution containing a predetermined concentration of test compound to a cup containing a kernel of corn in 16 g of sterile soil. This produces a soil concentration of 24 ppm.
25 After 1.5 to 2 hours of drying, five 4th instar corn rootworm larvae are added to the individual cups. Mortality is measured at 3-4 days by emptying the cup onto a pan and inspecting the soil for live rootworms.

Results for are reported in the following table. The
30 following abbreviations are used in the table:

CRW refers to corn rootworm

SAW refers to Southern armyworm

SM refers to twospotted spider mites

MA refers to melon aphids.

Compound	CRW RATE PPM	CRW RESULTS %	SAW SM & MA RATE	SAW RESULTS %	SM RESULTS %	MA RESULTS %
2	24.00	100	400	0	90	100
	12.00	0	200	0	0	0
3	24.00	0	400	60	90	90
	12.00	0	200	0	100	100
4	24.00	0	400	80	100	100
5	24.00	0	400	0	100	100
	12.00	0	200	0	90	100
6	24.00	0	400	0	0	0
7	24.00	100	400	0	80	100
	12.00	0	200	0	0	0
8	24.00	0	400	0	100	100
	12.00	0	200	100	100	100
9	24.00	0	400	0	0	0
11	24.00	0	400	0	80	40
	12.00	0	200	0	80	60
12	24.00	0	400	0	20	0
13	24.00	0	400	0	100	100
	12.00		200			
14	24.00	100	400	0	100	100
	12.00	0	200	0	80	80
15	24.00	100	400	0	0	40
	12.00	0	200	0	0	80
16	24.00	0	400	0	80	70
	12.00	0	200	0	0	0
19	24.00	0	400	0	0	0
48	24.00	0	400	0	0	0
50	24.00	0	400	0	0	0
51	24.00	0	400	0	0	60
55	24.00	0	400	0	90	30
56	24.00	0	400	0	0	0
	12.00	0	200	0	90	40
60	24.00	0	400	0	0	0
61	24.00	0	400	0	0	0
63	24.00	100	400	0	100	0
	12.00	100	200	0	100	0
69	24.00	0	400	0	0	0
71	24.00	0	400	0	0	0
72	24.00	0	400	0	80	80
	12.00	0	200	0	80	0
74	24.00	0	400	0	0	0
75	24.00	0	400	0	0	0
78	24.00	0	400	0	0	0
82	24.00	0	400	0	0	0
85	24.00	0	400	0	0	0
86	24.00	0	400	0	0	0
95	24.00	0	400	0	0	0
96	24.00	0	400	0	0	0
101	24.00	0	400	0	0	0
104	24.00	0	400	0	0	0
105	24.00	0	400	0	0	80
	12.00	0	200	0	0	0

Compound	CRW RATE PPM	CRW RESULTS %	SAW SM & MA RATE	SAW RESULTS %	SM RESULTS %	MA RESULTS %
106	24.00	80	400	0	0	60
	12.00	0	200	0	0	0
107	24.00	0	400	0	100	80
	12.00	0	200	0	100	80
123	24.00	0	400	0	0	0
124	24.00	0	400	40	70	90
	12.00	0	200	0	0	0
125	24.00	0	400	0	0	0
126	24.00	80	400	60	0	0
	12.00	0	200	0	0	0
147	24.00	0	400	0	0	0
148	24.00	0	400	100	0	0
	12.00	0	200	0	0	0
149	24.00	0	400	0	0	0
186	24.00	0	400	0	0	0
187	24.00	0	400	0	0	0
188	24.00	0	400	0	100	80
	12.00	0	200	0	0	0
189	24.00	0	400	0	0	0
190	24.00	0	400	0	0	90
191	24.00	0	400	0	0	0
192	24.00	0	400	0	100	100
	12.00	0	200	0	0	60
193	24.00	0	400	0	0	0
194	24.00	0	400	0	60	20
195	24.00	0	400	0	0	0
196	24.00	0	400	0	100	0
	12.00	100	200	0	90	0
		0		0	100	
197	24.00	0	400	0	0	0
198	24.00	0	400	0	0	0

Nematicide Utility

Some of the compounds of the present invention are also useful for reducing populations of nematodes. Accordingly, another aspect of the invention is a method of inhibiting a nematode population which comprises applying to a locus of a nematode an effective nematode inactivating amount of a compound of formula (1) or (10). The term "inhibiting a nematode" refers to a decrease in the numbers of living nematodes. The extent of reduction accomplished by a compound depends upon the application rate of the compound, the particular compound used, and the target species. At least a nematode-inactivating amount should be used. The term "nematode-inactivating amount" is used to describe the amount, which is sufficient to cause a measurable reduction in the treated nematode population.

The method is practiced in accordance with standard techniques for the application of nematicides. In general, good nematicidal activity can be expected at rates of 1-10 lbs/acre. The compound can be formulated as described below in the Compositions section. When formulated as dispersions, nematicides are typically applied as aqueous drenches around growing plants or applied incrementally via irrigation systems. When applied as granules, nematicides may be incorporated into the soil before planting, or applied in a band on top of a seed row, or broadcast and then incorporated into the soil, or used as a side dressing to an established crop.

Compositions

The compounds of formulas (1) and (10) are applied in the form of compositions which are important embodiments of the invention, and which comprise a compound of formula (1) or (10) and a phytologically-acceptable inert carrier. The compositions are either concentrated formulations which are dispersed in water for application, or are dust or granular formulations which are applied without further treatment. The

compositions are prepared according to procedures and formulae which are conventional in the agricultural chemical art, but which are novel and important because of the presence therein of the compounds of this invention. Some description of the
5 formulation of the compositions will be given, however, to assure that agricultural chemists can readily prepare any desired composition.

The dispersions in which the compounds are applied are most often aqueous suspensions or emulsions prepared from
10 concentrated formulations of the compounds. Such water-soluble, water-suspendable or emulsifiable formulations are either solids usually known as wettable powders, or liquids usually known as emulsifiable concentrates or aqueous suspensions. Wettable powders, which may be compacted to form
15 water dispersible granules, comprise an intimate mixture of the active compound, an inert carrier and surfactants. The concentration of the active compound is usually from about 10% to about 90% by weight. The inert carrier is usually chosen from among the attapulgite clays, the montmorillonite clays,
20 the diatomaceous earths, or the purified silicates. Effective surfactants, comprising from about 0.5% to about 10% of the wettable powder, are found among the sulfonated lignins, the condensed naphthalenesulfonates, the naphthalenesulfonates, the alkylbenzenesulfonates, the alkyl sulfates, and non-ionic
25 surfactants such as ethylene oxide adducts of alkyl phenols.

Emulsifiable concentrates of the compounds comprise a convenient concentration of a compound, such as from about 50 to about 500 grams per liter of liquid, equivalent to about 10% to about 50%, dissolved in an inert carrier which is
30 either a water miscible solvent or a mixture of water-immiscible organic solvent and emulsifiers. Useful organic solvents include aromatics, especially the xylenes, and the petroleum fractions, especially the high-boiling naphthalenic and olefinic portions of petroleum such as heavy
35 aromatic naphtha. Other organic solvents may also be used, such as the terpenic solvents including rosin derivatives,

aliphatic ketones such as cyclohexanone, and complex alcohols such as 2-ethoxyethanol. Suitable emulsifiers for emulsifiable concentrates are chosen from conventional nonionic surfactants, such as those discussed above.

5 Aqueous suspensions comprise suspensions of water-insoluble compounds of this invention, dispersed in an aqueous vehicle at a concentration in the range from about 5% to about 50% by weight. Suspensions are prepared by finely grinding the compound, and vigorously mixing it into a vehicle
10 comprised of water and

surfactants chosen from the same types discussed above. Inert ingredients, such as inorganic salts and synthetic or natural gums, may also be added, to increase the density and viscosity of the aqueous vehicle. It is often most effective to grind
15 and mix the compound at the same time by preparing the aqueous mixture, and homogenizing it in an implement such as a sand mill, ball mill, or piston-type homogenizer.

The compounds may also be applied as granular compositions, which are particularly useful for applications
20 to the soil. Granular compositions usually contain from about 0.5% to about 10% by weight of the compound, dispersed in an inert carrier which consists entirely or in large part of clay or a similar inexpensive substance. Such compositions are usually prepared by dissolving the compound in a suitable
25 solvent, and applying it to a granular carrier which has been pre-formed to the appropriate particle size, in the range of from about 0.5 to 3 mm. Such compositions may also be formulated by making a dough or paste of the carrier and compound, and crushing and drying to obtain the desired
30 granular particle size.

Dusts containing the compounds are prepared simply by intimately mixing the compound in powdered form with a suitable dusty agricultural carrier, such as kaolin clay, ground volcanic rock and the like. Dusts can suitably contain
35 from about 1% to about 10% of the compound.

It is equally practical, when desirable for any reason, to apply the compound in the form of a solution in an appropriate organic solvent, usually a bland petroleum oil, such as the spray oils, which are widely used in agricultural chemistry.

Insecticides and miticides are generally applied in the form of a dispersion of the active ingredient in a liquid carrier. It is conventional to refer to application rates in terms of the concentration of active ingredient in the carrier. The most widely used carrier is water.

The compounds of formula (1) and (10) can also be applied in the form of an aerosol composition. In such compositions the active compound is dissolved or dispersed in an inert carrier, which is a pressure-generating propellant mixture. The aerosol composition is packaged in a container from which the mixture is dispensed through an atomizing valve. Propellant mixtures comprise either low-boiling halocarbons, which may be mixed with organic solvents, or aqueous suspensions pressurized with inert gases or gaseous hydrocarbons.

The actual amount of compound to be applied to loci of insects and mites is not critical and can readily be determined by those skilled in the art in view of the examples above. In general, concentrations of from 10 ppm to 5000 ppm of compound are expected to provide good control. With many of the compounds, concentrations of from 100 to 1500 ppm will suffice. For field crops, such as soybeans and cotton, a suitable application rate for the compounds is about 0.5 to 1.5 lb/A, typically applied in 50 gal/A of spray formulation containing 1200 to 3600 ppm of compound. For citrus crops, a suitable application rate is from about 100 to 1500 gal/A spray formulation, which is a rate of 100 to 1000 ppm.

The locus to which a compound is applied can be any locus inhabited by an insect or arachnid, for example, vegetable crops, fruit and nut trees, grape vines, and ornamental plants. Inasmuch as many mite species are specific to a

particular host, the foregoing list of mite species provides exemplification of the wide range of settings in which the present compounds can be used.

Because of the unique ability of mite eggs to resist toxicant action, repeated applications may be desirable to control newly emerged larvae, as is true of other known acaricides.

The following formulations of compounds of the invention are typical of compositions useful in the practice of the present invention.

A. Emulsifiable Concentrate

Compound of Formula (1) or (10)	9.38%
"TOXIMUL D"	2.50%
(nonionic/anionic surfactant blend)	
"TOXIMUL H"	2.50%
(nonionic/anionic surfactant blend)	
"EXXON 200"	85.62%
(naphthalenic solvent)	

B. Emulsifiable Concentrate

Compound of Formula (1) or (10)	18.50%
"TOXIMUL D"	2.50%
"TOXIMUL H"	2.50%
"EXXON 200"	76.50%

C. Emulsifiable Concentrate

Compound of Formula (1) or (10)	12.50%
N-methylpyrrolidone	25.00%
"TOXIMUL D"	2.50%
"TOXIMUL H"	2.50%
"EXXON 200"	57.50%

D. Aqueous Suspension

	Compound of Formula (1) or (10)	12.00%
	"PLURONIC P-103"	1.50%
	(block copolymer of propylene oxide	
5	and ethylene oxide, surfactant)	
	"PROXEL GXL"	.05%
	(biocide/preservative)	
	"AF-100"	.20%
	(silicon based antifoam agent)	
10	"REAX 88B"	1.00%
	(lignosulfonate dispersing agent)	
	propylene glycol	10.00%
	veegum	.75%
	xanthan	.25%
15	water	74.25%

E. Aqueous Suspension

	Compound of Formula (1) or (10)	12.50%
	"MAKON 10" (10 moles ethyleneoxide	1.00%
20	nonylphenol surfactant)	
	"ZEOSYL 200" (silica)	1.00%
	"AF-100"	0.20%
	"AGRIWET FR" (surfactant)	3.00%
	2% xanthan hydrate	10.00%
25	water	72.30%

F. Aqueous Suspension

	Compound of Formula (1) or (10)	12.50%
	"MAKON 10"	1.50%
30	"ZEOSYL 200" (silica)	1.00%
	"AF-100"	0.20%
	"POLYFON H"	0.20%
	(lignosulfonate dispersing agent)	
	2% xanthan hydrate	10.00%
35	water	74.60%

G. Suspension Concentrate

	Compound of Formula (1) or (10)	10.20%
	"TERGITOL TMN-6"	3.40%
	"ZEOSYL 200"	0.90%
5	2% "KELZAN" solution	8.60%
	"AF-100"	0.20%
	water	76.70%

G. Wettable Powder

10	Compound of Formula (1) or (10)	25.80%
	"POLYFON H"	3.50%
	"SELLOGEN HR"	5.00%
	"STEPANOL ME DRY"	1.00%
	gum arabic	0.50%
15	"HISIL 233"	2.50%
	Barden clay	61.70%

H. Granules

	Compound of Formula (1) or (10)	5.0%
	propylene glycol	5.0%
20	Exxon 200	5.0%
	Florex 30/60 granular clay	85.0%

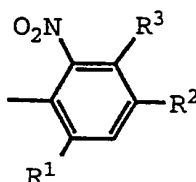
Claims

1. A method of inhibiting plant pathogens which comprises applying an effective amount of a compound of formula (1):



or a salt thereof, wherein:

Ar is a group of the formula



10 R^1 and R^2 are independently H, NO_2 , halo, $\text{C}_1\text{-C}_6$ alkyl, $\text{C}_1\text{-C}_6$ haloalkyl, $\text{C}_2\text{-C}_6$ alkenyl, $\text{C}_2\text{-C}_6$ alkynyl, $\text{C}_1\text{-C}_4$ alkylsulfonyl, phenylsulfonyl, substituted phenylsulfonyl, $\text{SO}_2\text{NR}^5\text{R}^6$, $\text{C}_1\text{-C}_4$ alkoxy, $\text{C}_1\text{-C}_4$ haloalkoxy, $\text{C}_1\text{-C}_4$ alkylthio, $\text{C}_1\text{-C}_4$ haloalkylthio, COOR^5 , or CN, provided R^1 is not CN, or CONR^5R^6 ;

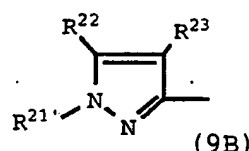
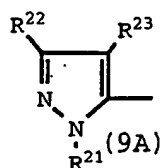
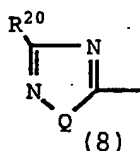
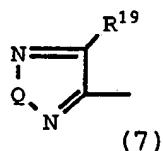
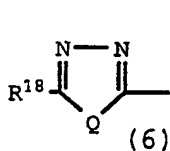
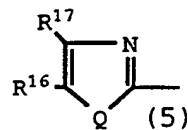
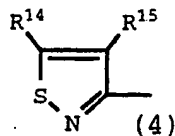
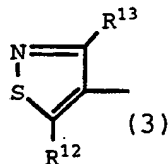
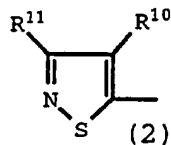
15 R^3 is H, halo, NR^5R^6 , $\text{C}_1\text{-C}_6$ haloalkyl, $\text{C}_1\text{-C}_6$ alkoxy, $\text{C}_1\text{-C}_6$ haloalkoxy, $\text{C}_1\text{-C}_6$ alkylthio, $\text{C}_1\text{-C}_6$ haloalkylthio, phenoxy, substituted phenoxy, phenylthio, substituted phenylthio, benzyloxy, substituted benzyloxy, benzylthio, or substituted benzylthio;

20 R^4 is H, COOR^7 , CONR^5R^6 , CHO, COR^7 , SO_2R^7 , or $\text{SO}_2\text{NR}^5\text{R}^6$;

25 R^5 and R^6 are H, $\text{C}_1\text{-C}_4$ alkyl, $\text{C}_3\text{-C}_7$ alkenyl, $\text{C}_3\text{-C}_7$ cycloalkyl or cycloalkenyl, or R^5 and R^6 together with the nitrogen atom to which they are attached form a 5-7 member ring containing up to three additional heteroatoms selected from O, N, and S;

R^7 is C₁-C₈ alkyl, C₃-C₈ alkenyl, C₃-C₈ branched alkyl, C₁-C₄ haloalkyl, aralkyl, phenyl, or substituted phenyl;

Het is a group selected from:

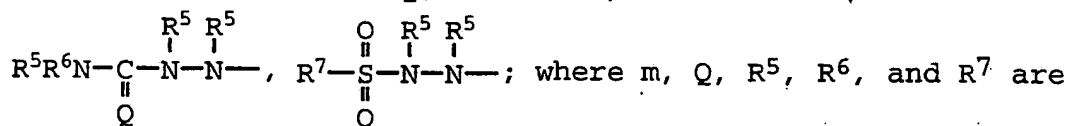
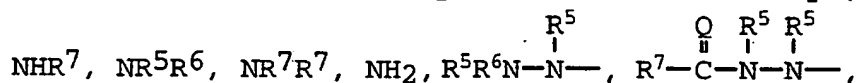


where

Q is S or O;

R^{10} is H, halo, C₁-C₈ alkyl, C₂-C₈ alkenyl, C₂-C₈ alkynyl, C₃-C₈ branched alkyl or alkenyl, C₃-C₇ cycloalkyl or cycloalkenyl, NO₂, CN, SCN, CO₂H, CONR⁵R⁶, CO₂R⁷, or S(O)_mR⁷ where m is 0, 1, or 2 and R⁵, R⁶, and R⁷ are as defined above.

R^{11} is H, halo, C₁-C₈ alkyl, C₂-C₈ alkenyl, C₂-C₈ alkynyl, C₃-C₈ branched alkyl or alkenyl, C₃-C₇ cycloalkyl or cycloalkenyl, aralkyl, (C₃-C₇ cycloalkyl)methyl, phenyl, substituted phenyl, pyridyl, substituted pyridyl, furyl, substituted furyl, thienyl, substituted thienyl, S(O)_mR⁷, OR⁷,



as defined above;

R^{12} is H, halo, CN, CO₂H, halo C₁-C₃ alkyl, phenyl, substituted phenyl, CONR⁵R⁶, or CO₂R⁷ where R⁵, R⁶, and R⁷ are as defined above;

R¹³ is H, halo, CN, CO₂H, halo C₁-C₃ alkyl, phenyl, substituted phenyl, CONR⁵R⁶, or CO₂R⁷ where R⁵, R⁶, and R⁷ are as defined above;

5 R¹⁴ is C₁-C₈ alkyl, C₂-C₈ alkenyl, C₂-C₈ alkynyl, C₃-C₈ branched alkyl or alkenyl, C₁-C₈ haloalkyl, phenyl, substituted phenyl, pyridyl, substituted pyridyl, thienyl, substituted thienyl, furyl, substituted furyl, or aralkyl;

R¹⁵ is H, halo, NO₂, CN, CO₂H, CONR⁵R⁶, or CO₂R⁷ where R⁵, R⁶, and R⁷ are as defined above;

10 R¹⁶ is H, halo, C₁-C₈ alkyl, C₂-C₈ alkenyl, C₂-C₈ alkynyl, C₃-C₆ branched alkyl or alkenyl, C₃-C₇ cycloalkyl or cycloalkenyl, C₁-C₈ haloalkyl, CN, NO₂, C₁-C₈ alkoxy, C₁-C₈ haloalkoxy, C₁-C₈ haloalkylthio, phenyl, substituted phenyl, thienyl, substituted thienyl, furyl, substituted furyl,
15 pyridyl, substituted pyridyl, aralkyl, phenoxy, or substituted phenoxy;

R¹⁷ is H, halo, C₁-C₈ alkyl, C₂-C₈ alkenyl, C₂-C₈ alkynyl, C₃-C₆ branched alkyl or alkenyl, C₃-C₇ cycloalkyl or cycloalkenyl, C₁-C₈ haloalkyl, CN, NO₂, C₁-C₈ alkoxy, C₁-C₈ haloalkoxy, C₁-C₈ haloalkylthio, phenyl, substituted phenyl,
20 thienyl, substituted thienyl, furyl, substituted furyl, pyridyl, substituted pyridyl, aralkyl, phenoxy, or substituted phenoxy;

R¹⁸ is H, halo, C₁-C₈ alkyl, C₂-C₈ alkenyl, C₂-C₈ alkynyl, C₃-C₆ branched alkyl or alkenyl, C₃-C₇ cycloalkyl or cycloalkenyl, C₁-C₈ haloalkyl, CN, NO₂, C₁-C₈ alkoxy, C₁-C₈ haloalkoxy, C₁-C₈ haloalkylthio, phenyl, substituted phenyl, thienyl, substituted thienyl, furyl, substituted furyl, pyridyl, substituted pyridyl, aralkyl, phenoxy, or substituted
25 phenoxy, S(O)_nR', where n is 0-3, and R' is H, C₁-C₈ alkyl, C₂-C₈ alkenyl, C₃-C₆ branched alkyl or alkenyl, phenyl, substituted phenyl, aralkyl, CF₃, or NR⁵R⁶ where R⁵ and R⁶ are
30 as defined above;

R¹⁹ is C₁-C₈ alkyl, C₂-C₈ alkenyl, C₂-C₈ alkynyl, C₃-C₆ branched alkyl or alkenyl, C₃-C₇ cycloalkyl or cycloalkenyl, phenyl, substituted phenyl, or aralkyl;

R²⁰ is H, halo, C₁-C₈ alkyl, C₂-C₈ alkenyl, C₂-C₈ alkynyl, C₃-C₆ branched alkyl or alkenyl, C₃-C₇ cycloalkyl or cycloalkenyl, C₁-C₆ haloalkyl, pyridyl, substituted pyridyl, furyl, substituted furyl, thienyl, substituted thienyl, phenyl, or substituted phenyl;

R²¹ and R^{21'} are C₁-C₈ alkyl, C₂-C₈ alkenyl, C₃-C₈ alkynyl, C₃-C₆ branched alkyl or alkenyl, C₃-C₇ cycloalkyl or cycloalkenyl, C₁-C₆ haloalkyl, pyridyl, substituted pyridyl, furyl, substituted furyl, thienyl, substituted thienyl, phenyl, substituted phenyl, aralkyl, COR⁷, CR^{7'}R^{7'}COOR⁷, CR^{7'}R^{7'}CONR⁵R⁶, or S(O)_mR⁷, where m, R⁵, R⁶, and R⁷ are as defined above, and R^{7'} is H or C₁-C₃ alkyl;

R²² is H, C₁-C₈ alkyl, C₂-C₈ alkenyl, C₂-C₈ alkynyl, C₃-C₈ branched alkyl or alkenyl, C₃-C₇ cycloalkyl or cycloalkenyl, C₁-C₆ haloalkyl, aralkyl, C₁-C₆ alkoxy, C₁-C₆ haloalkoxy, C₁-C₆ alkylthio, C₁-C₆ haloalkylthio, (C₅-C₇ cycloalkyl)methyl, halo, CN, SCN, NO₂, phenyl, substituted phenyl, phenoxy, substituted phenoxy, pyridyl, substituted pyridyl, furyl, substituted furyl, thienyl, substituted thienyl, or NR⁵R⁶ where R⁵ and R⁶ are as defined above; and

R²³ is H, halo, C₁-C₈ alkyl, C₂-C₈ alkenyl, C₂-C₈ alkynyl, C₃-C₈ branched alkyl or alkenyl, C₃-C₇ cycloalkyl or cycloalkenyl, C₁-C₆ haloalkyl, NO₂, CN, SCN, CO₂H, CONR⁵R⁶, CO₂R⁷, COR⁷, S(O)_mR⁷, phenyl, substituted phenyl, pyridyl, substituted pyridyl, furyl, substituted furyl, thienyl, substituted thienyl, or aralkyl, where m, R⁵, R⁶, and R⁷ are as defined above.

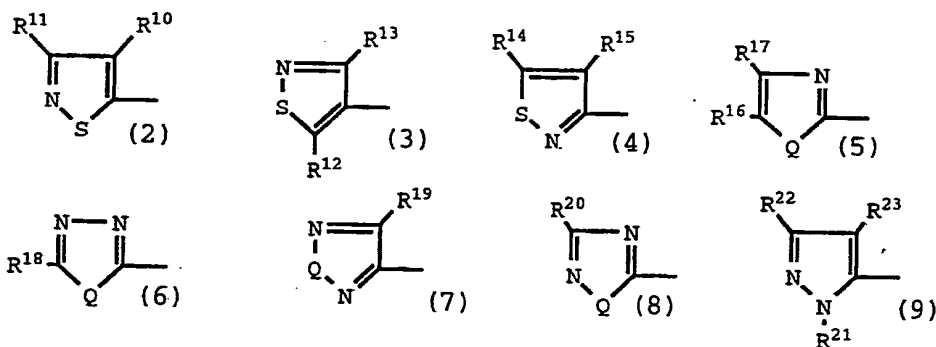
2. The method of inhibiting plant pathogens of claim 1 wherein the compound of formula (1) is one wherein:

R¹ and R² are independently H, NO₂, halo, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₂-C₆ alkenyl, C₂-C₆ alkynyl, C₁-C₄.

alkylsulfonyl, phenylsulfonyl, substituted phenylsulfonyl, $\text{SO}_2\text{NR}^5\text{R}^6$, $\text{C}_1\text{-C}_4$ alkoxy, $\text{C}_1\text{-C}_4$ haloalkoxy, $\text{C}_1\text{-C}_4$ alkylthio, $\text{C}_1\text{-C}_4$ haloalkylthio, COOR^5 , or CN, provided R^1 is not CN, or CONR^5R^6 , where R^5 and R^6 are H, $\text{C}_1\text{-C}_4$ alkyl, $\text{C}_3\text{-C}_7$ cycloalkyl;

5 R^3 is H, halo, $\text{C}_1\text{-C}_6$ haloalkyl, $\text{C}_1\text{-C}_6$ alkoxy, $\text{C}_1\text{-C}_6$ haloalkoxy, $\text{C}_1\text{-C}_6$ alkylthio, $\text{C}_1\text{-C}_6$ haloalkylthio, phenoxy, substituted phenoxy, phenylthio, substituted phenylthio, benzyloxy, substituted benzyloxy, benzylthio, or substituted benzylthio;

10 R^4 is H, COOR^7 , CONR^5R^6 , CHO, COR^7 , or SO_2R^7 , where R^5 and R^6 are as defined above and R^7 is $\text{C}_1\text{-C}_4$ alkyl, $\text{C}_1\text{-C}_4$ haloalkyl, benzyl, substituted benzyl, phenyl, or substituted phenyl;



15 R^{10} is H, halo, $\text{C}_1\text{-C}_6$ alkyl, $\text{C}_3\text{-C}_6$ branched alkyl, $\text{C}_3\text{-C}_6$ cycloalkyl, NO_2 , CN, CO_2H , CO_2Alk , CONR^5R^6 , where Alk is $\text{C}_1\text{-C}_6$ alkyl or halo $\text{C}_1\text{-C}_6$ alkyl, and where R^5 and R^6 are H, $\text{C}_1\text{-C}_4$ alkyl, or $\text{C}_3\text{-C}_7$ cycloalkyl;

20 R^{11} is halo, $\text{C}_1\text{-C}_6$ alkyl, $\text{C}_3\text{-C}_6$ branched alkyl, $\text{C}_3\text{-C}_6$ cycloalkyl, aralkyl, cyclohexylmethyl, phenyl, substituted phenyl, phenoxy, substituted phenoxy, pyridyl, furyl, or thienyl;

R^{12} is H, CO_2H , CO_2Alk , or CONR^5R^6 , where Alk, R^5 and R^6 are as defined above;

25 R^{13} is CN, CO_2H , CO_2Alk , or CONR^5R^6 , where Alk, R^5 and R^6 are as defined above;

R¹⁴ is C₁-C₆ alkyl, C₁-C₆ haloalkyl, phenyl, substituted phenyl, or aralkyl;

R¹⁵ is H, halo, NO₂, CN, CO₂H, CO₂Alk, CONR⁵R⁶, where Alk, R⁵ and R⁶ are as defined above;

5 R¹⁶ is H, halo, C₁-C₆ alkyl, C₃-C₆ branched alkyl, C₃-C₆ cycloalkyl, C₁-C₆ haloalkyl, CN, NO₂, C₁-C₆ alkoxy, C₁-C₆ haloalkoxy, C₁-C₆ haloalkylthio, phenyl, substituted phenyl, aralkyl, phenoxy, or substituted phenoxy;

10 R¹⁷ is H, halo, C₁-C₆ alkyl, C₃-C₆ branched alkyl, C₃-C₆ cycloalkyl, C₁-C₆ haloalkyl, CN, NO₂, C₁-C₆ alkoxy, C₁-C₆ haloalkoxy, phenyl, substituted phenyl, aralkyl, phenoxy, or substituted phenoxy;

15 R¹⁸ is H, halo, C₁-C₆ alkyl, C₃-C₆ branched alkyl, C₃-C₆ cycloalkyl, C₁-C₆ haloalkyl, CN, NO₂, C₁-C₆ alkoxy, C₁-C₆ haloalkoxy, phenyl, substituted phenyl, pyridyl, furyl, thienyl, aralkyl, phenoxy, substituted phenoxy, S(O)_nR', where n is 0-3, and R' is H, C₁-C₆ alkyl, C₃-C₆ branched alkyl, phenyl, substituted phenyl, CF₃, or NR⁵R⁶ and R⁵ and R⁶ are as defined above;

20 R¹⁹ is C₁-C₆ alkyl, C₃-C₆ branched alkyl, C₃-C₆ cycloalkyl, phenyl, substituted phenyl, or aralkyl;

R²⁰ is H, halo, C₁-C₆ alkyl, C₁-C₆ alkenyl, C₁-C₆ alkynyl, C₃-C₆ branched alkyl, C₃-C₆ cycloalkyl, C₁-C₆ haloalkyl, pyridyl, furyl, thienyl, phenyl, or substituted phenyl;

25 R²¹ is C₁-C₆ alkyl, C₃-C₆ branched alkyl, C₃-C₆ cycloalkyl, C₁-C₆ haloalkyl, pyridyl, furyl, thienyl, phenyl, substituted phenyl, aralkyl, or S(O)_mAlk, where m and Alk are as defined above;

30 R²² is C₁-C₆ alkyl, C₃-C₆ branched alkyl, C₃-C₆ cycloalkyl, aralkyl, C₁-C₆ alkoxy, C₁-C₆ haloalkoxy, C₁-C₆ alkylthio, C₁-C₆ haloalkylthio, cyclohexylmethyl, halo, NO₂,

NR⁵R⁶, phenyl, substituted phenyl, phenoxy, substituted phenoxy, pyridyl, furyl, thienyl; and

R²³ is H, halo, C₁-C₆ alkyl, C₃-C₆ branched alkyl, C₃-C₆ cycloalkyl, NO₂, CN, CO₂H, CO₂Alk, where Alk is C₁-C₆ alkyl or
 5 halo C₁-C₆ alkyl, or CONR⁵R⁶, where R⁵ and R⁶ are as defined above.

3. The method of inhibiting plant pathogens of claim 1 wherein the compound of formula (1) is one wherein Het is a group of formula (2).

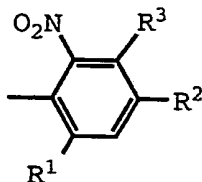
10 4. The method of inhibiting plant pathogens of claim 1 wherein the compound of formula (1) is selected from 4-bromo-3-methyl-N-(2,6-dinitro-4-(trifluoromethyl)phenyl)-5-isothiazolamine, 3-t-butyl-4-bromo-N-(2,6-dinitro-4-(trifluoromethyl)phenyl)isothiazol-5-amine, 4-bromo-3-cyano-N-
 15 (2,6-dinitro-4-(trifluoromethyl)phenyl)isothiazol-5-amine, 3-methyl-4-iodo-N-(2,6-dinitro-4-(trifluoromethyl)phenyl)isothiazol-5-amine, 3-t-butyl-4-bromo-N-(2,6-dinitro-4-cyanophenyl)isothiazol-5-amine. 1-(3-nitrophenyl)-4-phenyl-N-(2,6-dinitro-4-(trifluoro-
 20 methyl)phenyl)pyrazol-5-amine, 1-(3-trifluoro-methylphenyl)-4-cyano-N-(2,6-dinitro-4-(trifluoro-methyl)phenyl)pyrazol-5-amine, 1-(3-trifluoro-methylphenyl)-4-cyano-N-(2,6-dinitro-4-(trifluoro-methyl)phenyl)pyrazol-5-amine.

5. A compound of the formula (1):



or a salt thereof, wherein:

Ar is a group of the formula



R^1 and R^2 are independently H, NO_2 , halo, $\text{C}_1\text{-C}_6$ alkyl, $\text{C}_1\text{-C}_6$ haloalkyl, $\text{C}_2\text{-C}_6$ alkenyl, $\text{C}_2\text{-C}_6$ alkynyl, $\text{C}_1\text{-C}_4$ alkylsulfonyl, phenylsulfonyl, substituted phenylsulfonyl, $\text{SO}_2\text{NR}^5\text{R}^6$, $\text{C}_1\text{-C}_4$ alkoxy, $\text{C}_1\text{-C}_4$ haloalkoxy, $\text{C}_1\text{-C}_4$ alkylthio, $\text{C}_1\text{-C}_4$ haloalkylthio, COOR^5 , or CN, provided R^1 is not CN, or CONR^5R^6 ;

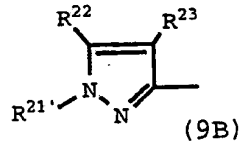
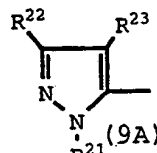
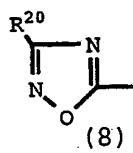
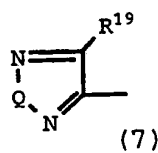
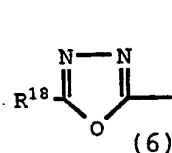
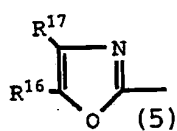
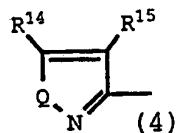
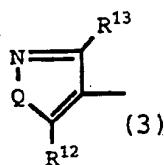
R^3 is H, halo, NR^5R^6 , $\text{C}_1\text{-C}_6$ haloalkyl, $\text{C}_1\text{-C}_6$ alkoxy, $\text{C}_1\text{-C}_6$ haloalkoxy, $\text{C}_1\text{-C}_6$ alkylthio, $\text{C}_1\text{-C}_6$ haloalkylthio, phenoxy, substituted phenoxy, phenylthio, substituted phenylthio, benzyloxy, substituted benzyloxy, benzylthio, or substituted benzylthio;

R^4 is H, COOR^7 , CONR^5R^6 , CHO, COR^7 , SO_2R^7 , or $\text{SO}_2\text{NR}^5\text{R}^6$;

R^5 and R^6 are H, $\text{C}_1\text{-C}_4$ alkyl, $\text{C}_3\text{-C}_7$ alkenyl, $\text{C}_3\text{-C}_7$ cycloalkyl or cycloalkenyl, or R^5 and R^6 together with the nitrogen atom to which they are attached form a 5-7 member ring containing up to three additional heteroatoms selected from O, N, and S;

R^7 is $\text{C}_1\text{-C}_8$ alkyl, $\text{C}_3\text{-C}_8$ alkenyl, $\text{C}_3\text{-C}_8$ branched alkyl, $\text{C}_1\text{-C}_4$ haloalkyl, aralkyl, phenyl, or substituted phenyl;

Het is a group selected from:



where

Q is S or O;

R¹² is H, halo, CN, CO₂H, halo C₁-C₃ alkyl, phenyl, substituted phenyl, CONR⁵R⁶, or CO₂R⁷ where R⁵, R⁶, and R⁷ are as defined above;

5 R¹³ is H, halo, CN, CO₂H, halo C₁-C₃ alkyl, phenyl, substituted phenyl, CONR⁵R⁶, or CO₂R⁷ where R⁵, R⁶, and R⁷ are as defined above;

10 R¹⁴ is C₁-C₈ alkyl, C₂-C₈ alkenyl, C₂-C₈ alkynyl, C₃-C₈ branched alkyl or alkenyl, C₁-C₈ haloalkyl, phenyl, substituted phenyl, pyridyl, substituted pyridyl, thienyl, substituted thienyl, furyl, substituted furyl, or aralkyl;

R¹⁵ is H, halo, NO₂, CN, CO₂H, CONR⁵R⁶, or CO₂R⁷ where R⁵, R⁶, and R⁷ are as defined above;

15 R¹⁶ is H, halo, C₁-C₈ alkyl, C₂-C₈ alkenyl, C₂-C₈ alkynyl, C₃-C₆ branched alkyl or alkenyl, C₃-C₇ cycloalkyl or cycloalkenyl, C₁-C₈ haloalkyl, CN, NO₂, C₁-C₈ alkoxy, C₁-C₈ haloalkoxy, C₁-C₈ haloalkylthio, phenyl, substituted phenyl, thienyl, substituted thienyl, furyl, substituted furyl, pyridyl, substituted pyridyl, aralkyl, phenoxy, or substituted phenoxy;

20 R¹⁷ is H, halo, C₁-C₈ alkyl, C₂-C₈ alkenyl, C₂-C₈ alkynyl, C₃-C₆ branched alkyl or alkenyl, C₃-C₇ cycloalkyl or cycloalkenyl, C₁-C₈ haloalkyl, CN, NO₂, C₁-C₈ alkoxy, C₁-C₈ haloalkoxy, C₁-C₈ haloalkylthio, phenyl, substituted phenyl, thienyl, substituted thienyl, furyl, substituted furyl, 25 pyridyl, substituted pyridyl, aralkyl, phenoxy, or substituted phenoxy;

30 R¹⁸ is H, halo, C₁-C₈ alkyl, C₂-C₈ alkenyl, C₂-C₈ alkynyl, C₃-C₆ branched alkyl or alkenyl, C₃-C₇ cycloalkyl or cycloalkenyl, C₁-C₈ haloalkyl, CN, NO₂, C₁-C₈ alkoxy, C₁-C₈ haloalkoxy, C₁-C₈ haloalkylthio, phenyl, substituted phenyl, thienyl, substituted thienyl, furyl, substituted furyl, pyridyl, substituted pyridyl, aralkyl, phenoxy, or substituted phenoxy, S(O)_nR', where n is 0-3, and R' is H, C₁-C₈ alkyl, C₂-C₈ alkenyl, C₃-C₆ branched alkyl or alkenyl, phenyl,

substituted phenyl, aralkyl, CF_3 , or NR^5R^6 where R^5 and R^6 are as defined above;

R^{19} is $\text{C}_1\text{-C}_8$ alkyl, $\text{C}_2\text{-C}_8$ alkenyl, $\text{C}_2\text{-C}_8$ alkynyl, $\text{C}_3\text{-C}_6$ branched alkyl or alkenyl, $\text{C}_3\text{-C}_7$ cycloalkyl or cycloalkenyl,
5 phenyl, substituted phenyl, or aralkyl;

R^{20} is H, halo, $\text{C}_1\text{-C}_8$ alkyl, $\text{C}_2\text{-C}_8$ alkenyl, $\text{C}_2\text{-C}_8$ alkynyl, $\text{C}_3\text{-C}_6$ branched alkyl or alkenyl, $\text{C}_3\text{-C}_7$ cycloalkyl or cycloalkenyl, $\text{C}_1\text{-C}_6$ haloalkyl, pyridyl, substituted pyridyl, furyl, substituted furyl, thienyl, substituted thienyl,
10 phenyl, or substituted phenyl;

R^{21} and $\text{R}^{21'}$ are $\text{C}_1\text{-C}_8$ alkyl, $\text{C}_2\text{-C}_8$ alkenyl, $\text{C}_3\text{-C}_8$ alkynyl, $\text{C}_3\text{-C}_6$ branched alkyl or alkenyl, $\text{C}_3\text{-C}_7$ cycloalkyl or cycloalkenyl, $\text{C}_1\text{-C}_6$ haloalkyl, pyridyl, substituted pyridyl, furyl, substituted furyl, thienyl, substituted thienyl,
15 phenyl, substituted phenyl, aralkyl, COR^7 , $\text{CR}^{7'}\text{R}^{7'}\text{COOR}^7$, $\text{CR}^{7'}\text{R}^{7'}\text{CONR}^5\text{R}^6$, or $\text{S(O)}_m\text{R}^7$, where m, R^5 , R^6 , and R^7 are as defined above, and $\text{R}^{7'}$ is H or $\text{C}_1\text{-C}_3$ alkyl;

R^{22} is H, $\text{C}_1\text{-C}_8$ alkyl, $\text{C}_2\text{-C}_8$ alkenyl, $\text{C}_2\text{-C}_8$ alkynyl, $\text{C}_3\text{-C}_8$ branched alkyl or alkenyl, $\text{C}_3\text{-C}_7$ cycloalkyl or
20 cycloalkenyl, $\text{C}_1\text{-C}_6$ haloalkyl, aralkyl, $\text{C}_1\text{-C}_6$ alkoxy, $\text{C}_1\text{-C}_6$ haloalkoxy, $\text{C}_1\text{-C}_6$ alkylthio, $\text{C}_1\text{-C}_6$ haloalkylthio, $(\text{C}_5\text{-C}_7$ cycloalkyl)methyl, halo, CN, SCN, NO_2 , phenyl, substituted phenyl, phenoxy, substituted phenoxy, pyridyl, substituted pyridyl, furyl, substituted furyl, thienyl, substituted
25 thienyl, or NR^5R^6 where R^5 and R^6 are as defined above; and

R^{23} is H, halo, $\text{C}_1\text{-C}_8$ alkyl, $\text{C}_2\text{-C}_8$ alkenyl, $\text{C}_2\text{-C}_8$ alkynyl, $\text{C}_3\text{-C}_8$ branched alkyl or alkenyl, $\text{C}_3\text{-C}_7$ cycloalkyl or cycloalkenyl, $\text{C}_1\text{-C}_6$ haloalkyl, NO_2 , CN, SCN, CO_2H , CONR^5R^6 , CO_2R^7 , COR^7 , $\text{S(O)}_m\text{R}^7$, phenyl, substituted phenyl, pyridyl, substituted pyridyl, furyl, substituted furyl, thienyl, substituted thienyl, or aralkyl, where m, R^5 , R^6 , and R^7 are as defined above;
30

provided that the following compounds are excluded:

- a) 5-methyl-2-(2,4,6-trinitroanilino)thiazole;
- b) N,4-dimethyl-2-(2,4,6-trinitroanilino)thiazole;
- c) 2-methyl-5-(2,4-dinitrophenylamino)-1,3,4-oxadiazole;
- d) N-methyl-5-trifluoromethyl-2-(2-chloro-4,6-
5 dinitroanilino)-1,3,4-thiadiazole;
- e) N-methyl-5-t-butyl-2-(2-chloro-4,6-dinitroanilino)-1,3,4-thiadiazole;
- f) N-acetyl-5-methyl-2-(4-bromo-2-nitroanilino)-1,3,4-thiadiazole;
- 10 g) N-acetyl-5-methyl-2-(4-methyl-2-nitroanilino)-1,3,4-thiadiazole;
- h) 3-(2,4-dinitroanilino)-4-nitro-5-phenylpyrazole; and
- i) 3-(2,6-dinitro-p-toluidino)-4-nitro-5-phenylpyrazole.

6. A compound of claim 5 wherein

- 15 R^1 and R^2 are independently H, NO_2 , halo, $\text{C}_1\text{-C}_6$ alkyl, $\text{C}_1\text{-C}_6$ haloalkyl, $\text{C}_2\text{-C}_6$ alkenyl, $\text{C}_2\text{-C}_6$ alkynyl, $\text{C}_1\text{-C}_4$ alkylsulfonyl, phenylsulfonyl, substituted phenylsulfonyl, $\text{SO}_2\text{NR}^5\text{R}^6$, $\text{C}_1\text{-C}_4$ alkoxy, $\text{C}_1\text{-C}_4$ haloalkoxy, $\text{C}_1\text{-C}_4$ alkylthio, $\text{C}_1\text{-C}_4$ haloalkylthio, COOR^5 , or CN, provided R^1 is not CN;

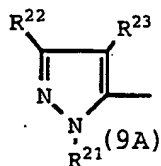
- 20 R^3 is H, halo, $\text{C}_1\text{-C}_6$ haloalkyl, $\text{C}_1\text{-C}_6$ alkoxy, $\text{C}_1\text{-C}_6$ haloalkoxy, $\text{C}_1\text{-C}_6$ alkylthio, $\text{C}_1\text{-C}_6$ haloalkylthio, phenoxy, substituted phenoxy, phenylthio, substituted phenylthio, benzyloxy, substituted benzyloxy, benzylthio, or substituted benzylthio;

- 25 R^4 is H, COOR^7 , CONR^5R^6 , CHO, COR^7 , or SO_2R^7 ;

R^5 and R^6 are H, $\text{C}_1\text{-C}_4$ alkyl, or $\text{C}_3\text{-C}_7$ cycloalkyl;

R^7 is $\text{C}_1\text{-C}_4$ alkyl, $\text{C}_1\text{-C}_4$ haloalkyl, benzyl, substituted benzyl, phenyl, or substituted phenyl;

Het is a group of the formula



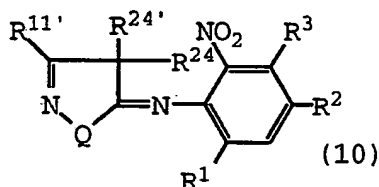
where

R^{21} is C_1 - C_6 alkyl, C_3 - C_6 branched alkyl, C_3 - C_6 cycloalkyl, C_1 - C_6 haloalkyl, pyridyl, furyl, thienyl, phenyl, substituted phenyl, aralkyl, or $S(O)_m$ Alk, where m is 0-2 and Alk is as defined above;

R^{22} is C_1 - C_6 alkyl, C_3 - C_6 branched alkyl, C_3 - C_6 cycloalkyl, aralkyl, C_1 - C_6 alkoxy, C_1 - C_6 haloalkoxy, C_1 - C_6 alkylthio, C_1 - C_6 haloalkylthio, cyclohexylmethyl, halo, NO_2 , NR^5R^6 , phenyl, substituted phenyl, phenoxy, substituted phenoxy, pyridyl, furyl, or thienyl; and

R^{23} is H, halo, C_1 - C_6 alkyl, C_3 - C_6 branched alkyl, C_3 - C_6 cycloalkyl, NO_2 , CN, CO_2H , CO_2 Alk, where Alk is C_1 - C_6 alkyl or halo C_1 - C_6 alkyl, or $CONR^5R^6$, where R^5 and R^6 are as defined above.

7. A compound of the formula (10):



wherein:

20 Q is S or O;

R^1 and R^2 are independently H, NO_2 , halo, C_1 - C_6 alkyl, C_1 - C_6 haloalkyl, C_2 - C_6 alkenyl, C_2 - C_6 alkynyl, C_1 - C_4 alkylsulfonyl, phenylsulfonyl, substituted phenylsulfonyl, $SO_2NR^5R^6$, C_1 - C_4 alkoxy, C_1 - C_4 haloalkoxy, C_1 - C_4 alkylthio, C_1 - C_4 haloalkylthio, $COOR^5$, $CONR^5R^6$, or CN, provided R^1 is not CN;

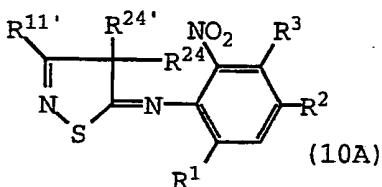
R^3 is H, halo, NR^5R^6 , C_1 - C_6 haloalkyl, C_1 - C_6 alkoxy, C_1 - C_6 haloalkoxy, C_1 - C_6 alkylthio, C_1 - C_6 haloalkylthio, phenoxy, substituted phenoxy, phenylthio, substituted phenylthio, benzyloxy, substituted benzyloxy, benzylthio, or substituted benzylthio;

R^5 and R^6 are H, C_1 - C_4 alkyl, C_3 - C_7 alkenyl, C_3 - C_7 cycloalkyl or cycloalkenyl, or R^5 and R^6 together with the nitrogen atom to which they are attached form a 5-7 member ring containing up to three additional heteroatoms selected from O, N, and S;

$R^{11'}$ is C_1 - C_8 alkyl, C_2 - C_8 alkenyl, C_2 - C_8 alkynyl, C_3 - C_8 branched alkyl or alkenyl, C_3 - C_7 cycloalkyl or cycloalkenyl, aralkyl, (C_3 - C_7 cycloalkyl)methyl, halo C_1 - C_8 alkyl, phenyl, substituted phenyl, pyridyl, substituted pyridyl, furyl, substituted furyl, thienyl, substituted thienyl; and

R^{24} and $R^{24'}$ are independently Cl or Br.

8. A compound of claim 7 having the formula (10A)



wherein:

R^1 and R^2 are independently H, NO_2 , halo, C_1 - C_6 alkyl, C_1 - C_6 haloalkyl, C_2 - C_6 alkenyl, C_2 - C_6 alkynyl, C_1 - C_4 alkylsulfonyl, phenylsulfonyl, substituted phenylsulfonyl, $SO_2NR^5R^6$, C_1 - C_4 alkoxy, C_1 - C_4 haloalkoxy, C_1 - C_4 alkylthio, C_1 - C_4 haloalkylthio, $COOR^5$, or CN, provided R^1 is not CN, or $CONR^5R^6$, where R^5 and R^6 are H, C_1 - C_4 alkyl, C_3 - C_7 cycloalkyl;

R^3 is H, halo, C_1 - C_6 haloalkyl, C_1 - C_6 alkoxy, C_1 - C_6 haloalkoxy, C_1 - C_6 alkylthio, C_1 - C_6 haloalkylthio, phenoxy, substituted phenoxy, phenylthio, substituted phenylthio, benzyloxy, substituted benzyloxy, benzylthio, or substituted benzylthio;

R¹¹ is C₁-C₆ alkyl, C₃-C₆ branched alkyl, C₃-C₆ cycloalkyl, aralkyl, cyclohexylmethyl, phenyl, substituted phenyl, pyridyl, furyl, or thienyl; and

R²⁴ and R^{24'} are independently Cl or Br.

5 9. A method of inhibiting plant pathogens which comprises applying an effective amount of a compound of any one of claims 5 to 8 to a locus of the pathogen.

10 10. A method of inhibiting a nematode population which comprises applying to the locus of a nematode, a nematode inactivating amount of a compound of any one of claims 5 to 8.

11. A method of inhibiting an insect or mite population which comprises applying to the locus of the insect or arachnid an effective insect or mite inactivating amount of a compound of any one of claims 5 to 8.

15 12. A pesticidal composition comprising a compound of any one of claims 5 to 8 in combination with an agriculturally acceptable carrier.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 93/02785

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 C07D275/02; A01N43/56; C07D271/10	C07D261/14; A01N43/74; C07D285/08	A01N43/80; C07D277/42; C07D231/38; A01N43/82 C07D285/12
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	C07D	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
Y	CA,A,2 051 297 (J.SCHUBERT ET AL) 21 March 1992 see page 20 - page 26; claims 1,2,5-8 & EP,A,0 478 974 8 April 1992 cited in the application ---	1-3,5,6, 9-12
Y	EP,A,0 406 700 (BASF AKTIENGESELLSCHAFT) 9 January 1991 see claims 1,4-6 ---	1-3,5,6, 9-12
Y	EP,A,0 135 472 (CIBA-GEIGY AG) 27 December 1985 see claims 1,8-12 ---	1-3,5,6, 9-12
	-/--	
<p>¹⁰ Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
15 JUNE 1993	21. 06. 93.	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	HENRY J.C.	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
Y	CHEMICAL ABSTRACTS, vol. 116, no. 13, 30 March 1992, Columbus, Ohio, US; abstract no. 123282q, page 326 ; see abstract & JP,A,3 261 771 (SHIONOGI AND CO.) 21 November 1991 ---	1-3,5,6, 9-12
X	CHEMICAL ABSTRACTS, vol. 110, no. 1, 2 January 1989, Columbus, Ohio, US; abstract no. 8104x, A. NAYAK ET AL 'Synthesis and fungicidal activities of some 2-pyrazolin-5-one derivatives' page 744 ; see abstract & ACTA CIENC. INDICA CHEM vol. 13, no. 1, 1987, pages 18 - 22 ---	1,5,9-12
X	ZEITSCHRIFT FÜR NATURFORSCHUNG, SECTIONC, BIOSCIENCES vol. 30C, 1975, TUBINGEN pages 183 - 189 G.SCHÄFER ET AL '2-Anilino-1,3,4-thiadiazoleHemmstoffe der oxidativen und photosynthetischen Phosphorylierung' see page 183 - page 186 ---	5
X	REVUE ROUMAINE CHIMIE vol. 14, no. 10, October 1969, BUCAREST pages 1285 - 1294 I.SIMITI ET AL 'Contribution à l'étude de quelques hétérocycles.XII L'halogénéation et la nitration de l'anilino-2-méthyl-5-thiodiazole-1,3,4' see pages1288-1290 -----	5

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9302785
SA 72272

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

15/06/93

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		AU-A- 3099784	31-01-85
		CA-A- 1218371	24-02-87
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